TREATMENT OF FERTILIZER INDUSTRY WASTE : A STUDY ON NITRIFICATION

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CERTIFICATE

This is to certify that the present work has been done under my supervision and the work has not been submitted else where for a degree.

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1. INTRODUCTION & SCOPE OF STUDY

Industrial wastes are the discharges from an establishment that prepares any material or article for the market. These differ from water supply received by the establishment and used in its operation. With the continuous increase of factories in various parts of country the problem of nuisance free disposal of wastes from factories is assuming great significance in India. Industrial wastes are the penalty paid by an industrial nation and are one of the inevitable problem connected with industrial progress. It has been estimated by U.S. public health service that over one hundred million dollors is lost annually due to pollution. The cost of water treatment, solely due to pollution, has been estimated to be 50 million dollars per year. Other losses included are those due to corrosion of metals both in pipe lines and industry, property depreciation, losses in recreational areas and losses in fishing industry.

These wastes from the industries can be put in to following groups according to their chracterstics.

The first type of waste is an acidic or basic waste, which can come from an industry such as steel mills or Chemical plants. These wastes when discharged in to the streams cause loss of aquatic life and made the stream water corrosive.

The second type of waste is an organic waste. Packing houses, dairies and Chemical plants are source of this type of waste. These wastes are unstable when discharged and require oxygen for stabilization. They take oxygen from receiving waters. Due to this consumption of oxygen anaerobic conditions develop

which create taste and odor problems. Besides, in many cases the desireable aquatic life of natural waters is destroyed.

The third type of waste is that containing oil and grease. The discharge of oil and grease to surface waters will decrease the rate of transfer of oxygen from atmosphere, create odors and damage ships, docks and recreational areas.

The fourth type of waste contains inert material which has no chemical effect on the stream, but presents the problem of sludge banks and silting.

Lastly, the waste water may contain substances which prove to be a public health hazard. Among such wastes would be included discharges from nuclear power establishments and wastes containing toxic metals, cynides, etc.

These industrial wastes are becoming conpicuous because the capacity of various water bodies, to assimilate waste material is fast getting exhausted. Further more, the water from streams and lakes is being used in greater quaintities and for increasing number of uses which demand greater purity of water.

In the nitrogenous fertilizer industry, certain amount of nitrogen finds its way in to the factory effluent. Such effluents generally contain the free ammonia, ammonium salts, urea and some times nitrates also. These are undesireable in river water if they are present beyond a certain concentration. Free ammonia and ammonium salts are harmful for fish population, while nitrate which may also be formed biologically from ammonia, when present in high concentration ($>$ 20 mg/l) in drinking water causes methamoglobinemia (1). Urea finding its way in natural bodies of water through industrial effluents is it self not as toxic as ammonia which is readily produced on its hydrolysis.

Due to nutritious nature of fertilizer waste there are ill effects due to fertilization of receiving waters. According to Flaigy and Reid (2) and Lackey (3) following are some of the ill effects.

(a) Growth of algae, among which some may be toxic in nature. These may also cause mechanical difficulties in treatment of water by filtration.

(b) Detoriation in water quality, such as an unpleasent apperance, taste and odor imparted by growing algae and obnoxious odors from algal decomposition. Such tastes and odor are usually difficult and expensive to remove.

(c) Build up of biochemical oxygen demand of water, due to a large concentration of algal cells which require oxygen for respiration during dark hours of the day. Besides, some algal crop may die. A dead crop behaves like decomposiable organic matter and therefore exerts oxygen demand.

The problem of disposal of fertilizer waste is assuming wide intrest in our country because of an increasing number of fertilizer factories. Treatment of fertilizer waste water require special consideration because they usually contain high concentration of ammonical nitrogen. Due to this reason it is not possible to treat it by conventional treatment processes which are used for treating domestic or municipal sewage. The nitrogen from waste is removed due to synthesis into algal or bacterial protoplasm, which inturn is seperated from the liquid streams. For this a balanced substrate and suitable envoirnmental conditions for their growth are required. However, such a treatment is not feasiable for fertilizer waste water as factor sustaining

synthesis of bacterial or algal growth, viz., carbon source, light, phosphorous etc. may be limiting or absent. Besides, disposal of synthesized cellular material would pose a problem.

The processes which may remove nitrogen from a fertilizer waste can be listed as :

1. Stripping.
2. Ion Exchange.
3. Electrochemical treatment.
4. Electrodialysis.
5. Land application.
6. Nitrification and denitrification system.

Stripping is a modification of the aeration process used for the removal of gases and volatile substances in the water. It has been observed at pH above 10 over 85% of the ammonia present in waste water can be removed by air stripping (4). But its applicability and economey has to be find out for the removal of nitrogen from fertilizer waste.

The processes of ion exchange, electrochemical treatment and electrodialysis are not feasiable due to high cost (4).

In the process of land application, the water percolates through soil. It has been found that the two most important factors which control the movement of nitrogen through the soils are physical adsorption and biological action (5). Physical adsorption appears to be the principal mechanism in the removal of nitrogen in the form of ammonium ion. This process requires large land area.

The nitrogen from a waste can be removed by the process of nitrification and denitrification. Johnson and Schroepfer (6) reported that process of nitrification and denitrification has a

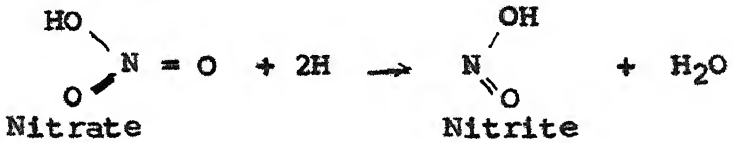
good potential for attaining higher removal of nitrogen. However, the process of nitrification and denitrification has yet to achieve popularity in biological waste treatment. The process can be summarized by the following two reactions :

(a) Nitrification

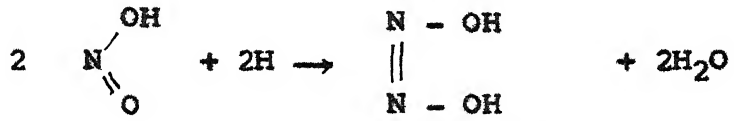
$$NH_4^+ + 1.5\ O_2 \xrightarrow[\text{Organisms}]{\text{Nitrifying}} 2H^+ + H_2O + NO_2^-$$

$$NO_2^- + 0.5\ O_2 \xrightarrow[\text{Organisms}]{\text{Nitrifying}} NO_3^-$$

(b) Denitrification

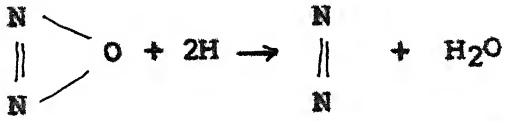


Nitrate Nitrite



Hyponitrite

Nitrous Oxide (gas)



Nitrogen (gas)

The application of such a treatment process, gives a scope for a considerable amount of exploratory research. More-ever, the findings in this area will help in improvement and design of plants handling waste waters containing high concentration of nitrogen.

The present study has been directed towards the process of nitrification. It has been observed by Majumdar (7) that nitrifying

bacteria can multiply well if a supporting medium is provided to them. This supporting medium provides surface where the nitrifying bacteria can stick and multiply. If the surface area provided is large a larger number of nitrifying bacteria can be maintained in a reactor provided sufficient food and air is avilable to them, Thus improving the efficiency of the system. Specifically the aim of the investigation was to corelate the surface area of the supporting medium in a reacter with the rate of nitrification and to evaluate parameters describing the growth of nitrifying organisms.

2. LITERATURE REVIEW

2.1 Chracterstics of Fertilizer Wastes

A detailed study of the chracterstics of chemical fertilizer industry waste has not been carried out so far.

The composite effluent may contain ammonia, spent caustic soda and potash, mono eathanolamine, acids, methanol, higher alcohals, fluorides, carbon slurry, lubricants, nitrogen in oxidized forms, phosphate etc., depending on the raw materials and manufacturing process.

The chracterstics of the wastewater from two plants in India are tabulated (7). Vide tables 1 and 2. The phenols and cyanides probably derive from the raw material coal.

TABLE 1

CHRACTERSTICS OF WASTEWATER AT SINDHRI FERTILIZER UNIT, SINDRI

Description	Period	No. of reading	Constituents	Analysis in ppm (average)
Stream I	May to June 1965	15	Total phenol	1.6
			Cyanide as CN	1.5
			Amm. Nitrogen	88
			Suspended solids	3369
			Oil	8.2
			Flow in mgd.	2.1
Stream II	May to June 1965	15	Phenol	0.7
			Cyanide	1.2
			Amm. Nitrogen	315.0
			Suspended Solids	398.0
			Oil	11.5
			Flow in mgd.	7.8

TABLE 2

ESTIMATED CHRACTERSTICS OF UREA PLANT, KANPUR (U.P.)

Item	kg/hr.	ppm
Volume 107 m^3/hr		
Temperature 45°C		
Urea	114.7	1065
NH_3	149.3	1410
CO_2	200.5	1860
Other dissolved Solids	136.4	1280
Total dissolved solids	251.1	2345
Suspended solids	-	-
Total solids	251.1	2345
Ammonical Nitrogen		1160

2.2 Forms of Nitrogen and its ammount in sewage

The primary source of nitrogen in sewage are the end products of nitrogen metabolism in the man. Industrial waste can also contribute some amount of nitrogen in municipal waste. However, in the average municipality, industrial waste do not produce large amount of proteinaceous nitrogen. Nitrogenous compound in sewage may be represented by aminoacids and protein. Other compounds of nitrogen which might be present are uric acid, ammonium salts, creatinine, free amines and amides. But the largest single source of nitrogen is urea as is clear from table 3 which shows the consitituents of normal urine (8).

TABLE 3

CONSTITUTENTS OF NORMAL URINE

Constituents	gm/l.
Urea	25
Uric acid	0.6
Ammonia	0.6
Creatinine	1.5
Undetermined nitrogen	0.6
Sugar	Traces
Ketone bodies	Traces
Pigments	

Domestic sewage have been analyzed by many workers. Nave and Buswell (9) found that urea and ammonia nitrogen was 90% of the total sewage nitrogen. Heukelekian and Balmat (10) seperated sewage solids, organic nitrogenous material was hydrolyzed and the amino acids were determined. The ancino acids accounted for 65 to 81% of the organic nitrogen. Sastry, Subrahmanyam and Pillai(1 found 0.36 to 1.01 mg. of free amino acids and 65 to 91.3 mg. of tota amino acids per gram of total solids. Delwiche (12) concluded that organic consitituents of sewage, exclusive of urea, constitute normally 10% of the total nitrogen. Table 4 represents chemical analysis (only of nitrogenous compound) of sewages of various strengths (13).

TABLE 4

TYPICAL SANITARY CHEMICAL ANALYSIS OF SEWAGE (13)
(Nitrogenous compound only)

Constituents	Strong (mg/l.)	Medium (mg/l.)	Weak (mg/l.)
Nitrogen total	85	50	25
Organic	35	20	10
Free ammonia	50	30	15
Nitrites (RNO_2)	0.10	0.05	0
Nitrates (RNO_3)	0.40	0.20	0.10

For Indian cities Gharpure (14) has given different values of nitrogenous constituents in domestic sewage and these values are given in table 5.

TABLE 5

ANALYSIS OF SEWAGE
(Nitrogenous Constituents only)

Particulars	Places in India			
	Poona	Kanpur	Lucknow	Allahabad
	Parts per 100,000			
Free and saline ammonia	2.65	2.43	6.24	3.2
Alluminoid ammonia	0.65	1.80	2.30	1.5
Nitrite nitrogen	nil	nil	nil	nil
Nitrate nitrogen	nil	nil	nil	nil
Total nitrogen	3.30	4.23	8.54	4.7

If a comparision is made between the amount of nitrogen in sewage and fertilizer plant effluent, we see that the amount of nitrogen in sewage is very less as compared to fertilizer wastes.

2.3 Nitrogen removal from waste water

During the process of sewage treatment, some percent nitrogen is removed in the sedimentation process. Babbitt (13) and Whurmann (15) have published data showing that approximately 20 to 30 percent of nitrogen in the raw waste was removed by primary treatment consisting of sedimentation. The further reduction of nitrogen takes place in the biological treatment units like activated sludge or trickling filter. The removal in these system is due to

(a) Utilization of nitrogen for the synthesis of new cells.

(b) The process of nitrification and denitrification.

It is generally believed that the removal of the various constituents in the sewage by a biological sludge is normally accomplished by an initial adsorption of the material on the sludge particles followed by oxidation or assimilation of the material by the bacterial cell. Heukelkian (16) and Ingoles (17) found that the effect of adsorption in the removal of ammonia nitrogen was of minor importance. They also found little removal of amino acids by adsorption mechanism.

It is generally believed that the nitrogen must be in the amino acid form to be available to the bacteria in building protoplasm. Therefore, proteinaceous material must be hydrolyzed to the amino acids and ammonia nitrogen synthesized in to amino acid molecules before being available to the bacteria.

In the second process, removal is due to biological oxidation of nitrogenous compounds to nitrites and nitrates followed by conversion to nitrogen gas. This two stage process is known as

nitrification and denitrification which involves aerobic and anaerobic biological stages of reactions. In the process of nitrification the ammonia is oxidized biologically to nitrite and nitrate. During the process of denitrification nitrate is used as hydrogen acceptor for emergy yielding oxidative reaction of micro-organisms instead of oxygen, and N_2 or N_2O gas produced. This nitrate reduction is also known as dissimilatory nitrate reduction. Besides this reduction of nitrate can take place for the building of cell protein, which is known as assimilatory nitrate reduction.

The process of denitrification is due to denitrifying activities of genus Pseudomonas. Two organisms have been isolated. (a) Ps. pyocyanea which produced N_2O and N_2. (2) Ps. atutseri which produces mainly N_2 gas. Apart from these two organisms, there is one more distinct specie, Ps. denitrifican, which is responsible for reduction of N_2O to N_2 gas.

Biochemical nitrification and denitrification process actually occure in many conventional biological treatment plants. Where nitrites or nitrates are found in the effluent, at some place in process, the biochemical denitrification process undoubtly is at work.

Number of studies have been carried out for the removal of nitrogen from wastewater by the process of nitrification and denitrification. Ludzack and Ettinger (18) found that associate nitrification and denitrification was the potential method for providing superior effluents from an oxygen demand and nitrogen stand point at lower air requirement in usual tank capacity. Snell (19), Whurmann (20) and Bringmann (21) have shown removal

of nitrogen by the process of nitrification and denitrification. Whurmann (20) shown that the elimination rate of nitrogen was decreased by a decrease in aeration period. Heukelekian (22) observed that presence of organic matter in sewage does not influence the rate of nitrification of sewage. Johnson (23) observed that for active nitrification, the period of aeration must exceed a minimum value which was the function of the concentration of active sludge, temperature and the strength of sewage. He also found that the minimum period of aeration was roughly proportional to the 5-day BOD of the sewage applied and will decrease very roughly in the inverse proportion to the concentration of sludge in aeration units. It was estimated that with a normal domestic waste, complete nitrification will require approximately 50 percent more air then that required for BOD stabilization.

Haltrich (24) showed with his batch test and continuous flow pilot plant studies that organic industrial waste containing nitrate can be purified by the activated sludge process. This was achieved by denitrification, i.e. mixing the nitrate containing waste with the activated sludge in an unaerated stage to reduce the nitrate. He found that if the wastewater contains organic impurities acting as a hydrogen donar, denitrification proceeds rapidly, and the detention time in a plant with denitrification was no greater than in a conventional activated sludge plant. Without hydrogen donars, the detention time was more.

In summary the process of nitrification and denitrification can remove nitrogen. However, such removals have been observed

in municipal waste which have small amount of nitrogen as compared to fertilizer wastes.

2.4 The nitrifying organisms

The biological conversion of ammonia to nitrite and nitrate was first found by Schloesing and Müntz (25) in france. The nitrifying organisms will be present in soil and in wastewater. According to Warrington (25) a minute seeding (0.1 gm of soil in a flask of sterile ammonium sulfate solution) was sufficient to start nitrification. The soil taken from more then 18" in depth was found by him to be inactive seeding. According to Delwike (12) nitrifying bacteria are present in wastewater containing ammonium ion provided oxygen is readily avilable. Nitrifying bacteria, although generally are soil bacteria, may also be found in water in swamps, streams and lakes (25).

2.4.1 Process of nitrification

The term "Nitrification" refers to the oxidation of the ammonium ion or other nitrogenous compound to nitrite or nitrate by autotrophic organism, usually in soil system, or other media containing mixed flora (27). The whole process of nitrification can be split up in two steps.

(a) The oxidation of ammonia to nitrite which is also known as nitrosofication or the first stage of nitrification.

$$NH_4^+ + 1.5\ O_2 \ \text{—} \ 2H^+ + H_2O + NO_2^-$$

(b) Oxidation of nitrite to nitrate which is known as nitrification or second stage of nitrification.

$$NO_2^- + 0.5\ O_2 \ \text{—} \ NO_3^-$$

During the process of nitrification the medium becomes acidic because the NH_4^+ cation is being converted to NO_3^- anion and hydrogen ions (25). Addition of $CaCO_3$ therefore, promotes nitrification by providing a reserve of base (25). It also gives calcium for their growth.

The organisms which oxidises NH_4^+ ion to nitrite are (a) Nitrosomonas (b) Nitrosococcus (c) Nitrospira (d) Nitrocysist (e) Nitrogloea. Organism capable of oxidizing nitrite to nitrate are (a) Nitro bacter (b) Nitrocystis.

Existing information regarding the most common species of Nitrosomonas and Nitrobacter is summarized below in table 6 and 7 (28).

TABLE 6

Nitrosomonas europaea

Taxonomy:

Order - Pseudomonadales

Suborder - Pseudomona-dinene

Family - Nitrobacteraceae

Genus - Nitrosomonas

Specie - europaea

Cellular chracterstics:

Morphology - Rods, almost ellipscidal

Motility - Motile, Flagella polar, 4 to 8 μ in length, occuring single or in a mass.

Size - 0.9 to 1.0 by 1.1 to 1.8 microns

Habitat - Soil, widely distributed.

Cultural chracterstics:

Aqueous media with salts - grows readily at bottom in soft masses around $MgCO_3$.

Silica gel colonies - small, compact, brownish well defined.

Physiological chracterstics:

Biochemical action

Ammonia - oxidized to nitrite

Ammonium salt - oxidized to nitrite.

Growth factors.

Oxygen - aerobic

Nutrition - Strictly autotrphic, medium must contain ammonium salt such as ammonium sulfate, $MgCO_3$ and pottasium phosphate.

Inhibition - Chelating agents inhibit formation of nitri from ammonia.

TABLE 7

Nitrobacter winogradskyi

Taxonomy:

Order - Pseudomonadales

Suborder - Pseudomonadineae

Family - Nitrobacteraceae

Genus - Nitrobacter

Specie - winogradskyi

Cellular chracterstics:

Morphology - short rods

Motility - Non motile

Membrane - Gelatinous

Staining - Gram negative, difficult to stain.

Size - 0.6 to 0.8 by 1.0 to 1.2 microns

Habitat - Soil (alkaline)

Cultural chracterstics:

Washed agar colonies - In a week to 10 days, small circ to irregular, light brown, becom darker.

Washed agar slant - Greyish, streak in 7 to 10 days.

Inorganic solution medium - Flocculent, sediment after 10 da senstive to ammonium salt under alkaline condition.

Silica gel - Small dense colonics

Mineral broth - Sediment in one week to 10 days

Physiological chracterstics:

Biochemical action

Nitrate - Formed from nitrite

Ammonium - Oxidized to nitrites

Growth factors

Oxygen - aerobic

Temperature - 25 to 28°C

Nutrition - Strictly autotrophic

There are two general areas of conflicting evidence with reference to the autotrophic nature of the nitrifying bacteria. The first of these two is that whether these nitrifiers are capable to exist on an organic energy source and the second is whether other organism normally considered hetrotrophs are capab. of nitrification. There is no evidence for the extensive utiliza

of organic compounds for energy by Nitrosomonas or Nitrobacter. Bömeke (27) pointed out that in the absence of ammonium ion there was some endogenous respiration of both Nitrosomonas and Nitrobacter which would indicate a limited ability to oxidize organic substrates. He showed that nitrogen containing substances caused a slight increase in respiration of resting cells. The inability to grow on organic media free of ammonia or nitri was used a test for the purity of nitrifying cultures by Gibbs

Repeated references have been made to the inhibitory effects of organic compounds on the growth of the nitrifiers. Winogradesky & Omeliansky and Meyerhof (27) demonstrated that many organic compounds were inhibitory in varying concentration However, the claim that organic compounds in general are inhibitory is not permissiable. Many worker such as Davenport (27) and Jensen (27) have supported this claim with their work.

Besides, these autotrophic nitrifying bacteria, there are some hetrotrophic bacteria which can oxidize ammonia to nitrite. These belong to genera of Pseudomonas, Streptomyces and Nocarclia. The oxidation of nitrite to nitrate appears to be carried out only by Nitrobacter (27). However, several species of soil fungi (Aspergillus flavus, Penicillum (sp), Cephlosporiu sp) appear to be capable of carrying out both steps oxidizing organic nitrogen to nitrite and nitrate.

The nitrifying bacteria differ significantly in their behaviour in soil and in pure cultures. The most significant difference is their response to the effect of organic matter. It was shown that peptone was far less inhibitory in sand than

in solution culture (30). It has also been shown that soil, even after ingition, was a far better medium for supporting nitrification as compared to sand (30). Cinders were more effective than sand and brick. It was observed that the presence of colloids influenced the bacterial behaviour. The nitrifying bacteria isolated from different soils have different nitrifying capacities.

One of the major difficulties in culturing these nitrifying bacteria resides in their extreme senstivity of excess substrate when in culture. Meyerhof (25) found that Nitrosomonas was inhibited by its substrate i.e. ammonia and Nitrobacter was inhibited by its substrate i.e. nitrite. It was observed that there was a sharp substrate concentration optimum for both types of bacteria and was quite contradictory to the normal behaviour of most other organism with their respective substrate. Again it was observed that Nitrobacter was inhibited by free ammonia and they developed when nitrosomonas lowered the ammonia level (25). Siddiqi etal (31) used 0.10 M ammonia nitrogen concentration for the elimination of nitrification in BOD determination. Hofman and Lees (32) demonstrated that for maximum rate of nitrification the concentration should be 0.005 M and that very definite inhibition occured at 0.10 M ammonia nitrogen.

2.4.2 The nitrogen carbon ratio

It was observed that nitrifying bacteria were not highly active as compared to other bacteria. A Nitrosomonas cells takes nearly an hour to produce twice its weight of nitrite (25).

Various worker have given different values for the ratio of N:C (i.e. NH_4^+ oxidized: CO_2 reduced). Winogradsky (27)

measured this ratio and found it to be 35, while with similar method Nelson (25) obtained this value as 15. On the other hand Hes (25) obtained this value close 33 while Bomke (25) 35 to 53.

The value of N:C for Nitrobacter was found to be 135 by Winogradsky (33) and Meyerhof obtained this value as 101.

From these values it has been concluded (33) that old cultures will give higher values for this ratio i.e. they are less efficient in assimilating carbon.

From this ratio of N:C, thermodynamic efficiency of nitrifiers can be calculated. Meyerhof (33) found free energy efficiency of Notrosomonas as 5.9% when N:C was 35. For Nitrobacter this value was 9%. That is, the energy liberated by ammonia oxidation only 5.9% is used for the reduction of CO_2.

2.4.3 Effect of pH

Nitrification may be observed over a wide range of pH (5-13), but the actual range with an isolated organisms seems to be dependent on the pH of soil from which it is isolated. Nitrification can be observed at as low a pH as 4.1.

Mehyerhof (25) found optimum pH for Nitrosomonas and Nitrobacter as 8.5 to 8.8. Hofman & Lees (32) found the optimum pH for Nitrosomonas as 8.5. Alexender and Aleem (34) reported that Nitrobacter agillis was most active at pH 8.0. Majumdar (7) reported the optimum pH for Nitrosomonas in between 7.5 to 8.3, where as the optimum pH range for Nitrobacter was in between 8.0 to 8.5.

2.4.4 Effect of Temperature

The majority of known chemical reaction are increased in rate by increase in temperature. In biological system this increase in rate is limited because at higher temperature the enzymes begin to be denatured.

Knowles et al (35) found that growth rate constant was considerably increased between the temperature 8 to 23°C. They suggested the following equation for Nitrosomonas.

$$\log_{10} Km = 0.0413\ T - 0.944$$

where Km is growth rate constant in day^{-1}.

T is temperature in °C.

The implication of this equation is that the growth rate constant increases by about 9.5% of existing value per degree centigrade increase in temperature. The equation for Nitrobacter was given as follows:

$$\log_{10} K_b = 0.0255\ T - 0.0492$$

where K_b is growth constant for Nitrobacter in day^{-1}.

The temperature coefficient was obtained as 5.9% per degree which means that growth rate constant for Nitrobacter was 50% greater than that of Nitrosomonas.

Buswell et al (35) found Km increasing from about 0.5 day^{-1} at 15°C to about 2 day^{-1} at 32°C. The temperature coefficient was found as 8.2% per degree. The magnitude of Km at a given temperature is dependent on the pH value of medium and its composition. Painter and Loveless (35) obtained maximum value of Km as 0.7 to 0.9 day^{-1} at 25°C and pH 7.6 to 8.0 in a batch culture and beyond this range they found that growth rate decreases.

Knowles et al (35) found that the saturation (Michaclis) constants for NH_3-N (Nitrosomonas) and NO_2-N (Nitrobacter) were of the same order below 20°C, but the values for both substrate were increased with the rise in temperature. The rate of increase in saturation constant for Nitrobacter was higher than that for Nitrosomonas. They suggested the following equation for change in value of saturation constant with temperature.

$$\log_{10} x = 0.051\ T - 1.158$$

where x is saturation constant for ammonia in mg/l.

For Nitrobacter the relation was as follows

$$\log_{10} Y = 0.063\ T - 1.149$$

where Y is saturation constant for nitrite in mg/l.

These relations correspond to an increase in saturation constant of about 11.8% of existing value per °C increase in temperature for ammonia and 14.5% of existing value per °C increase in temperature for nitrite.

The optimum temperature for nitrification is dependent on the site of isolation of the organism but in temperate regions it is approximately 25°C (30). Schloesing and Müntz obtained optimum temperature at 30°C to 35°C (25).

2.5 Kinetics of fixed film biological reactors

In Fixed film reactors, like other biological processes, the action of micro-organism for the removal of soluble organic compounds is necessary. In deriving a mathematical model for a fixed film reactor, two primary facts must be recognized. The first is that the organisms and substrate do not occupy a common volume. Therefore, any relation between organisms and substrate must be made on a mass basis. The second is that the entire mass of attached micro-organism

is not active in the removal of substrate. Kornegay (36) presented a mathematical model on the following assumptions.

(a) Complete mixing was acheived in liquid phase.

(b) Substrate utilization due to source other than the attached microbial film was small and negligible.

(c) Removal was described by a saturation function which incarporated the effects of diffusion and growth rate.

Consider an annular reactor in which the attached micro-organisms utilize oxygen and nutrients from the completely mixed liquid phase[36]. Let the flow rate is $F(L^3/T)$ and initial substrate concentration is S_o (M/L^3). The substrate concentration in the reactor and in the effluent are same and is equal to S_1 (M/L^3). The substrate utilized by the microbial film is equal to S_o-S_1. The mass of film responsible for this utilization is equal to the product of surface area (L^2), the concentration of organisms in the biological film X (M/L^3) and depth of active film of organisms, d, (L). During the period of film accumulation, the actual film thickness, h, is less than the active thickness, d, and the active mass of film is equal to

$$M_o = (A)(h)(X) \quad \ldots \quad \ldots \quad \ldots 1$$

When the actual film thickness, h, is equal to or greater than the active film thickness, d, the active mass is constant and equal to

$$M_o = (A)(X))(d) \quad \ldots \quad \ldots \quad \ldots 2$$

The substrate balance can be given as

$$\text{Change} = \text{Input} - \text{Output} - \text{Utilization}$$

$$(dM_s/dt)_{net} = FS_o - FS_1 - (dM_s/dt)_{utilization} \ldots 3$$

Where M_s denotes the mass of substrate.

Monod showed that substrate utilization and the corresponding organism growth may be related by the following expression.

$$(dM_s/dt)_{utilization} = 1/y(dM_o/dt)_{growth} \quad \ldots \quad 4$$

where y is the yield constant.

The rate of change in mass of organism may be expressed as the product of specific growth rate constant and the mass of organism M_o i.e.

$$(dM_o/dt)_{growth} = \mu M_o \quad \ldots \quad \ldots \quad \ldots \quad 5$$

where μ is the specific growth rate (T^{-1})

From equations 3,4 & 5

$$(dM_s/dt)_{net} = FS_o - FS_1 - \mu/y \; M_o \quad \ldots \quad \ldots \quad 6$$

When the actual film thickness h, is less than active thickness, d, equation 6 may be written as

$$(dM_s/dt)_{net} = FS_o - FS_1 - \mu/y \; (A)(X)(h) \quad \ldots \quad 7$$

The accumulation of film is continuous till the actual thickness, h, equals or exceeds the active thickness, d. The active mass of organisms then becomes constant and steady state is reached with respect to substrate utilization at this stage

$$(dM_s/dt)_{net} = 0 \quad \ldots \quad \ldots \quad \ldots \quad 8$$

and equation 7 becomes

$$F(S_o - S_1) = \mu/y \; (A)(X)(d)$$

From Monod expression the value of u can be given as

$$\mu = \mu_{max} \; S_1 / K_s + S_1 \quad \ldots \quad \ldots \quad 9$$

Where μ_{max} is maximum specific growth rate (T^{-1}) and K_s is saturation constant (M/L^3).

By putting the value of μ from equation 9 in equation 8

$$F(S_o - S_1) = \frac{\mu_{max} S_1}{K_s + S_1} \quad \frac{(A)(X)(d)}{Y} \quad \ldots\ldots \quad \ldots\ldots \quad 10$$

By rearranging equation 10

$$\frac{(A)(X)(d)}{Y F(S_o - S_1)} = \frac{K_s}{\mu_{max}} \cdot \frac{1}{S_1} + \frac{1}{\mu_{max}} \quad \ldots \quad \ldots\ldots \quad 11$$

The left hand side expression of the equation 11 is equal to reciprocal of specific growth rate. By knowing the film thickness, d, surface area, A, and organism concentration X, the specific growth rate can be calculated from different values of F and corrosponding values of S_1.

When reciprocal of specific growth is ploted against the reciprocal of the substrate concentration, a linear plot resulted. The slope of line is equal to K_s/μ_{max} and the ordinate intercept is $1/\mu_{max}$. From these K_s and μ_{max} can be determined.

3. MATERIALS AND METHODS

3.1 Experimental Design and Equipment

Important factors for the growth of nitrifying bacteria are (a) Supply of oxygen (b) Supply of substrate (ammonia) (c) Proper pH value (d) Supply of carbon source. While planning the experiment, due consideration was given to all these various aspects.

3.1.1 Source of nitrifying bacteria

The nitrifying bacteria are always present in domestic sewage. These bacteria find their way from soil. Domestic sewage is usually a good source for both types of nitrifying bacteria.

For all experiments in this study, nitrifying seed was developed by aerating domestic sewage for few days. In the sewage the inorganic medium (described in the following section), substrate (ammonium chloride) and phosphate buffer (to keep the pH at desired level) were added before starting aeration. The convertion of ammonia nitrogen in to nitrite and nitrate, indicated that sufficient number of both Nitrosomonas and Nitrobacter had developed. This sewage was utilized as the source of nitrifying bacteria.

3.1.2 Inorganic medium

The nitrifying bacteria are strict autotrophs, they live only on inorganic medium. In essence, they synthesize complex compounds, composing their protoplasm, from inorganic salts and utlize carbonates or carbondioxide as their carbon source (26).

Table 8 gives the details of the inorganic medium used by Siddiqi et al (31). The same medium was provided in all the experiments in this study.

TABLE 8

INORGANIC MEDIUM

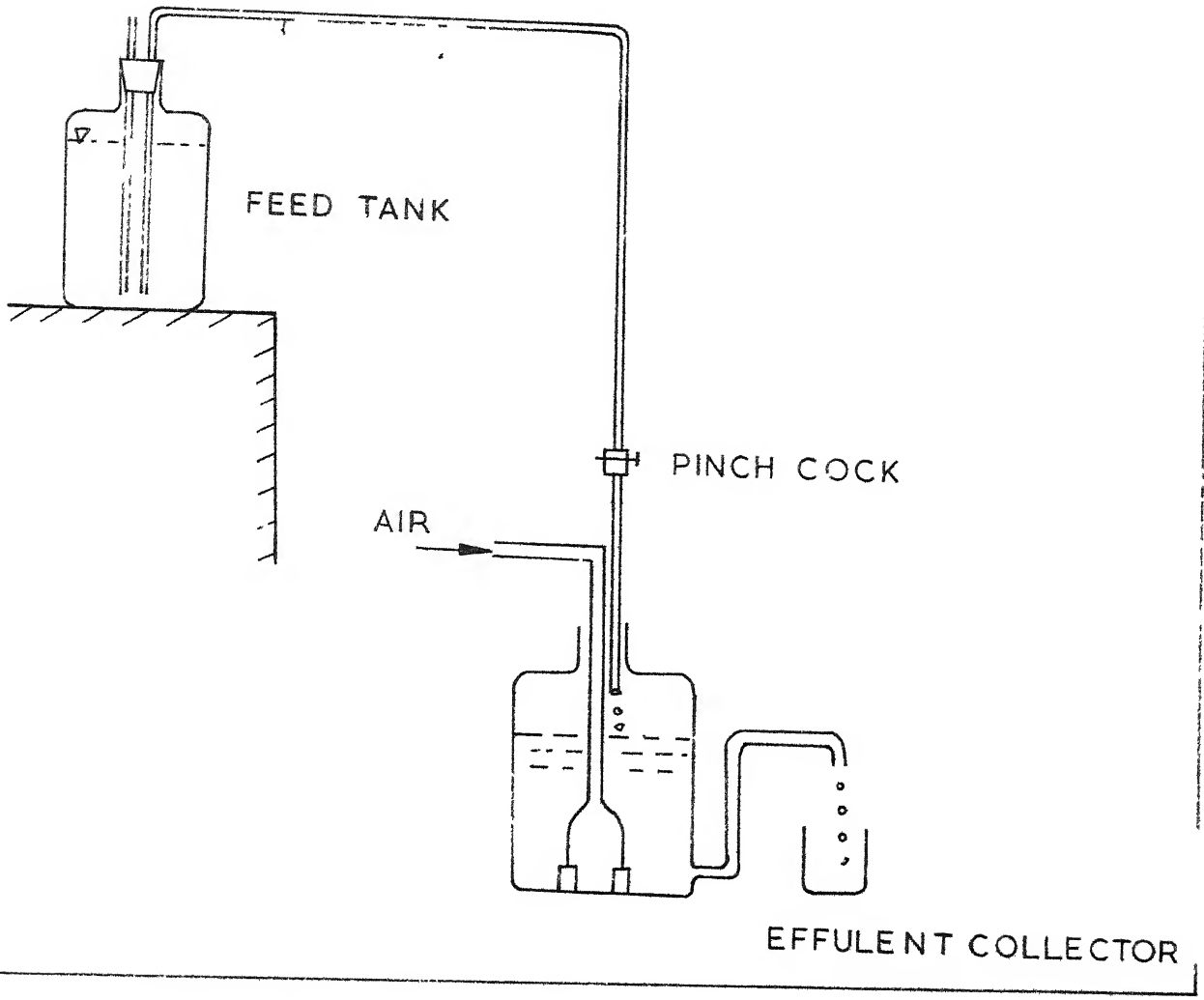
$FeCl_3 . 6 H_2O$	0.125 mg/l.
$MgSO_4 . 7 H_2O$	25.0 mg/l.
$K_2H PO_4$	3.0 mg/l.
$CaCO_3$	50.0 mg/l.
$Na HCO_3$	250.0 mg/l.
NH_4Cl	as desired

3.1.3 Nitrification in a continuous flow reactor

As the waste water from the Fertilizer industry is a continuous one, this study was carried out for finding out the rate of nitrification in a continuous flow and completely mixed reacter at different flows. The NH_3-N concentration in the feed was kept as 750 mg/liter.

3.1.3.1 Nitrification in reactor without any supporting medium

Fig. 1 represents the laboratory set up of the reactor vessel along with other accessories. The liquid volume in the reactor was maintained at 5 liters by keeping a constant level of over flow. The compressed air was supplied through two diffusers. The pH was maintained 8.0 by using 0.1 M phosphate buffer. The flow rate from feed tank was controlled by means of a screw clamp fitted in to the tube from the feed tank and was held constant by using a constant head siphon as shown in figure 1.



IG. I DETAILS OF CONTINUOUS FLOW REACTOR VESSEL WITHOUT SUPPORTING MEDIUM

The samples were collected after every 12 hours and analyzed for NH_3-N, NO_2-N and NO_3-N.

3.1.3.2 Nitrification in reactor with supporting medium

Since the nitrifying bacteria grow better if a supporting medium is provided, in a reactor a supporting medium was provided. The experiments were conducted in two phases.

In first phase sand was used as a supporting medium. Fig. 2 represents the laboratory set up. Two such reactors were run at the same time. In one reactor the thickness of sand bed was kept 4 cm while in other the thickness was 8 cm. The sand used in both the reactors was from the same source. The sand was first passed from seive No. 18 and then from seive no. 25. The sand retained on the seive no. 25 was used for the experiment. Fig. 3 shows the seive analysis for this sand.

The liquid volume in both the reactors was kept 5 liters. The pH was maintained at 8.0 by using the phosphate buffer. The compressed air was supplied through diffusers.

The flow in one reactor was regulated by using a electrolytic pump with gas generator (36) as shown in fig. 4. The flow in the other reactor was regulated by constant head siphon. The tanks were kept covered from top for avoiding evoporation losses. The samples were collected after every 12 hours and were analyzed for NH_3-N, NO_2-N and NO_3-N.

In the second phase of study, straw was used as a supporting medium. Ten grams of the straw was filled in between a folded piece of wire gauze having 2 cm. x 2 cm. opening, in the form of thin layer. Fig. 5 represents the laboratory set up for this study. Two such reactors were used. In one reactor only one

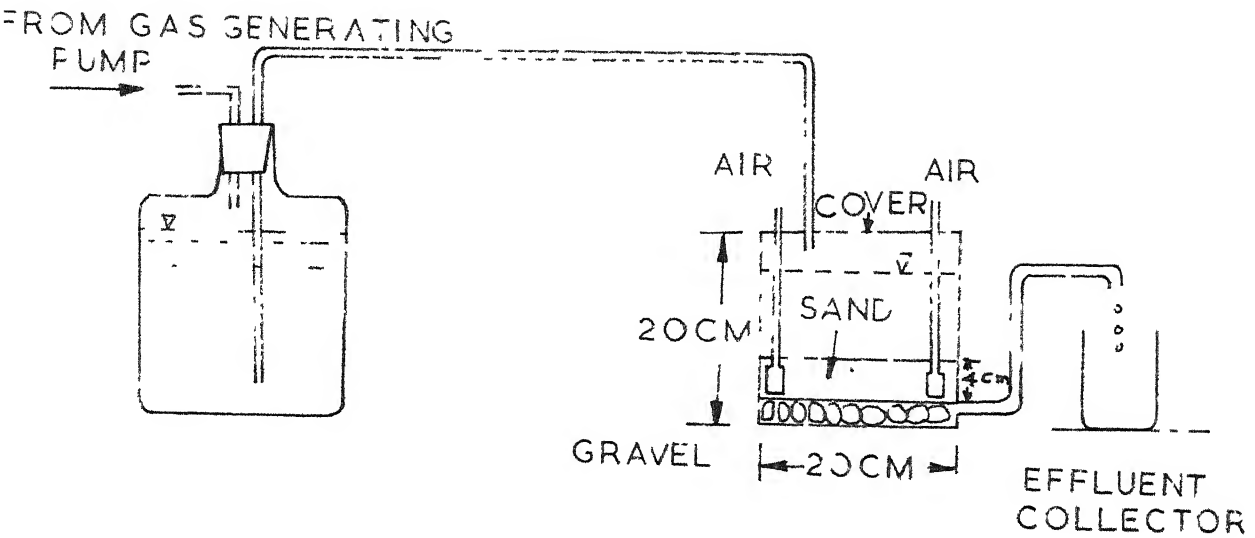
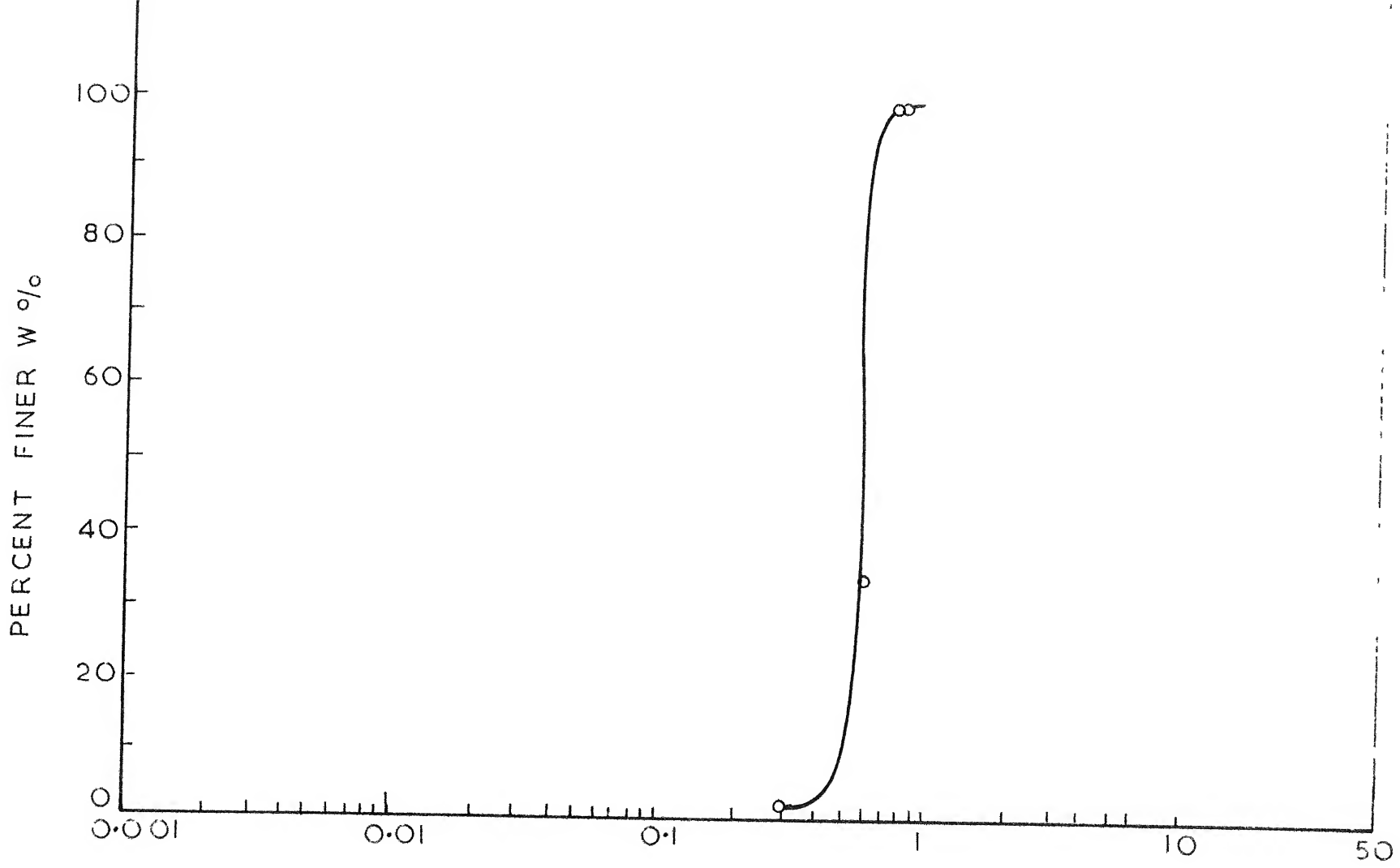
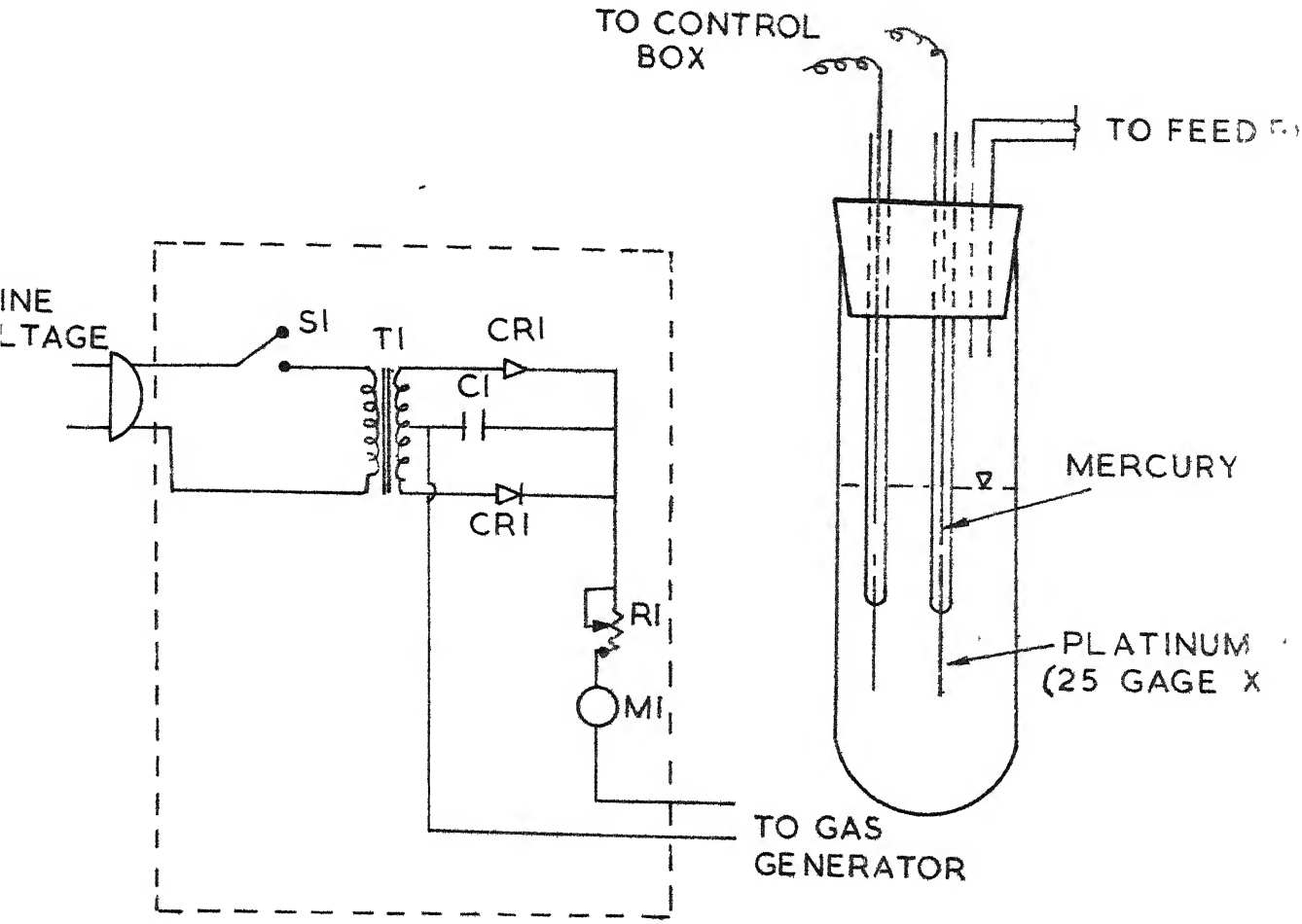


FIG. 2 DETAILS OF CONTINUOUS FLOW REACTER VESSEL WITH SUPPORTING MEDIUM AS A SAND



$$u_c = \frac{D_{60}}{D_{10}} = \frac{0{\cdot}5}{0{\cdot}5} = \sim 1$$

FIG.3 SEIVE ANALYSIS OF USED SAND



S_1 - SPST SWITCH, 1 AMP, T_1 12·6 V CENTRE TAP TRANSFORME
CR_{12} 500 ma SILICAN RECTIFIER, R_1 300Ω, 5 WHATT M_1 - O-
METER C_1 - 50 UF, 25 V ELECTROLYTIC CAPACITOR

FIG 4 DE TAILS OF ELECTROLYTIC PUMP

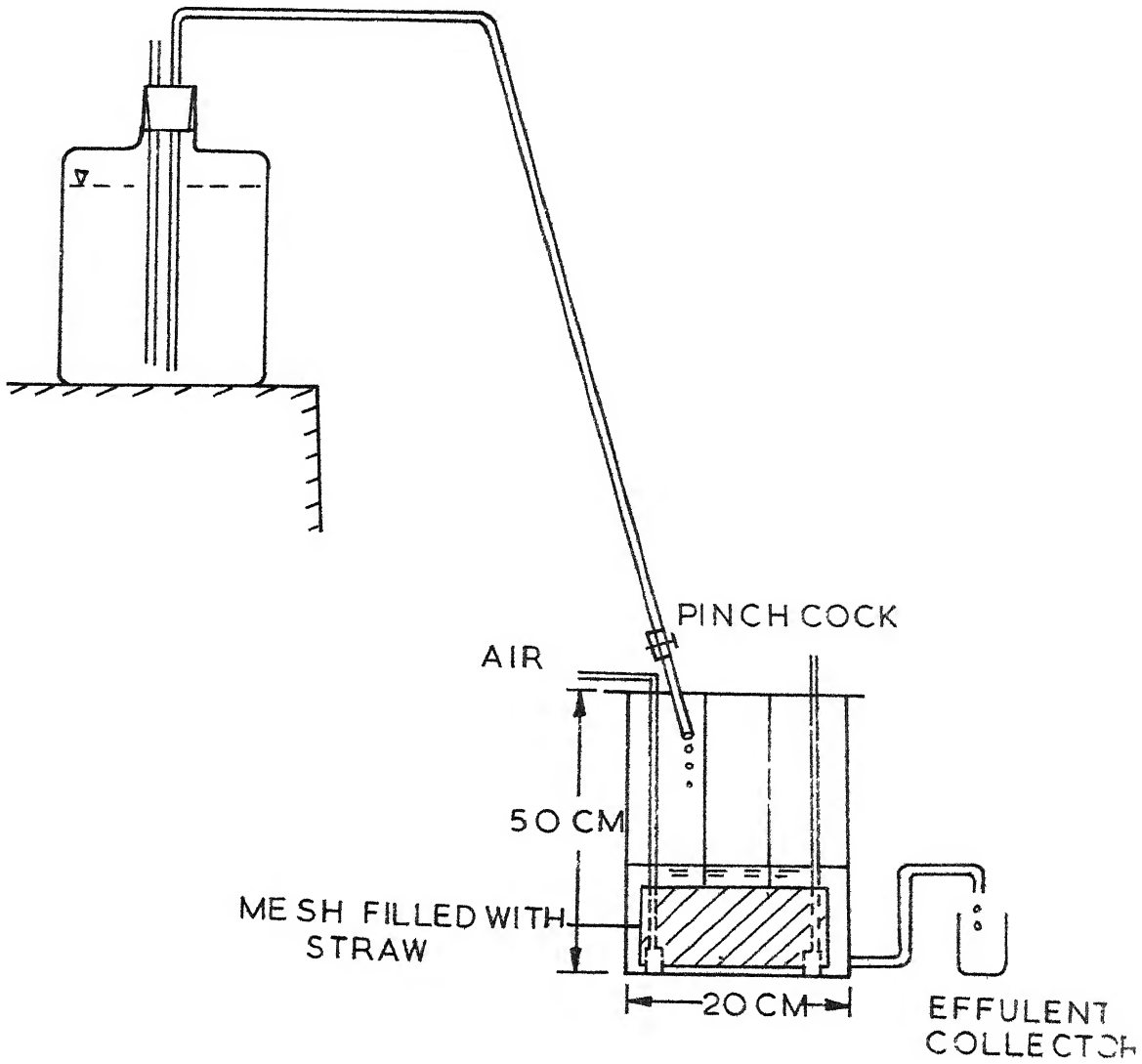


FIG 5 DETAILS OF CONTINUOUS FLOW REACTOR VESSEL WI
SUPPORTING MEDIUM AS PACKING STRAW

straw bed was suspended and in other reactor two similar bed were kept. These beds were kept below the liquid surface in both the cases. The other conditions were the same. The flow was regulated by the same methods as stated previously.

The samples were collected after every 12 hours and were analyzed for NH_3-N, NO_2-N and NO_3-N.

3.2 Analytical Techniquies

3.2.1 Ammonia Nitrogen, Nitrite Nitrogen and Nitrate Nitrog

NH_3-N, NO_2-N and NO_3-N were determined by the method of direct nesslerization, sulfanilic acid naphthylamine hydrochloride and Brucine method respectively as described in Standard methods

The standard calibration curve for NH_3-N, NO_2-N and NO_3-N are shown in fig. 6, fig.7 and fig. 8 respectively.

3.2.2 pH

pH of the samples was measured by means of an Expandomati pH meter[1].

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1. Manufacturer, Beckman Instruments Inc.
Scientific and process Instruments division,
Fullerton, California 92634.

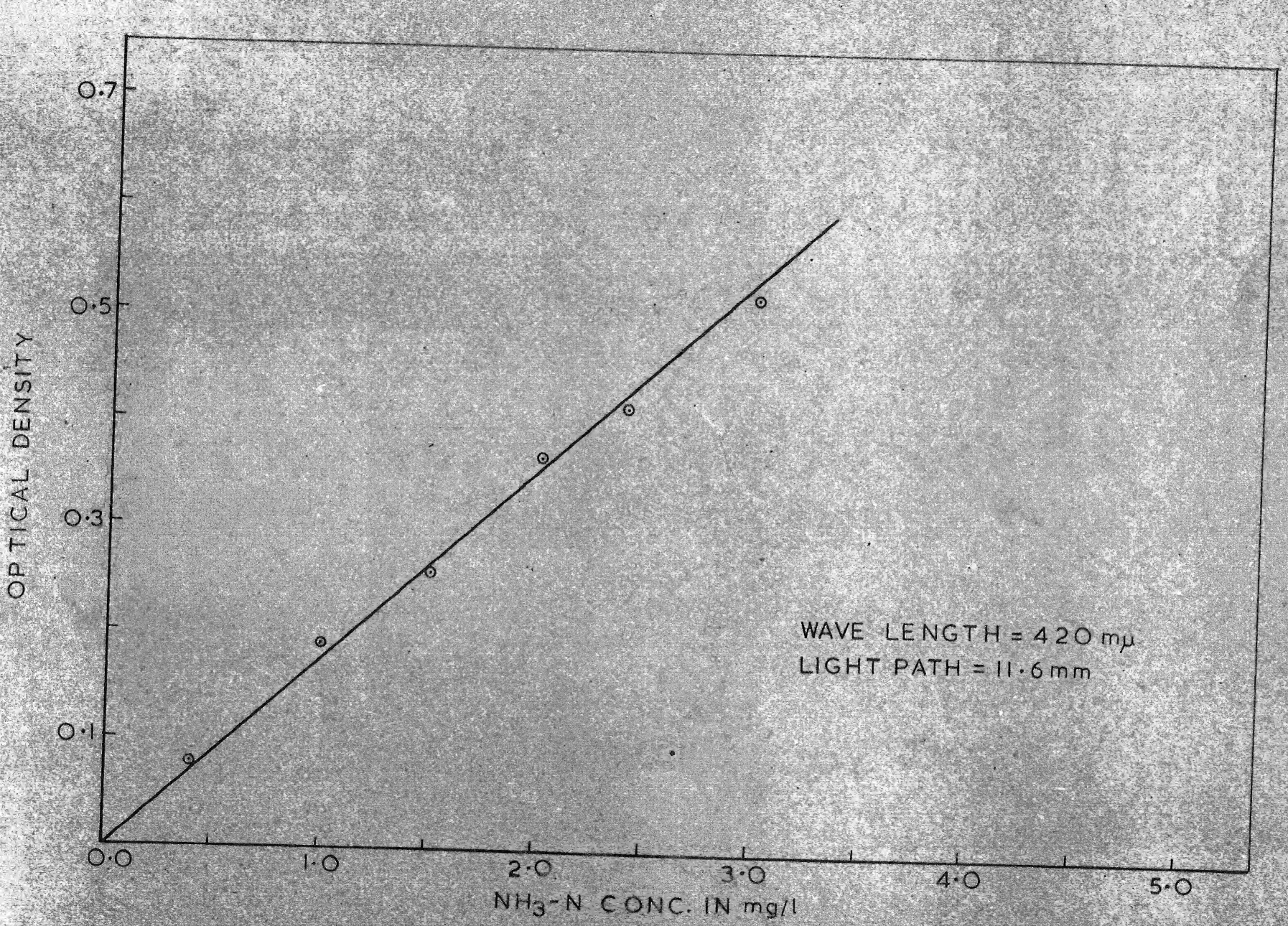


FIG 6 STANDARD CALIBRATION CURVE FOR NH_3-N

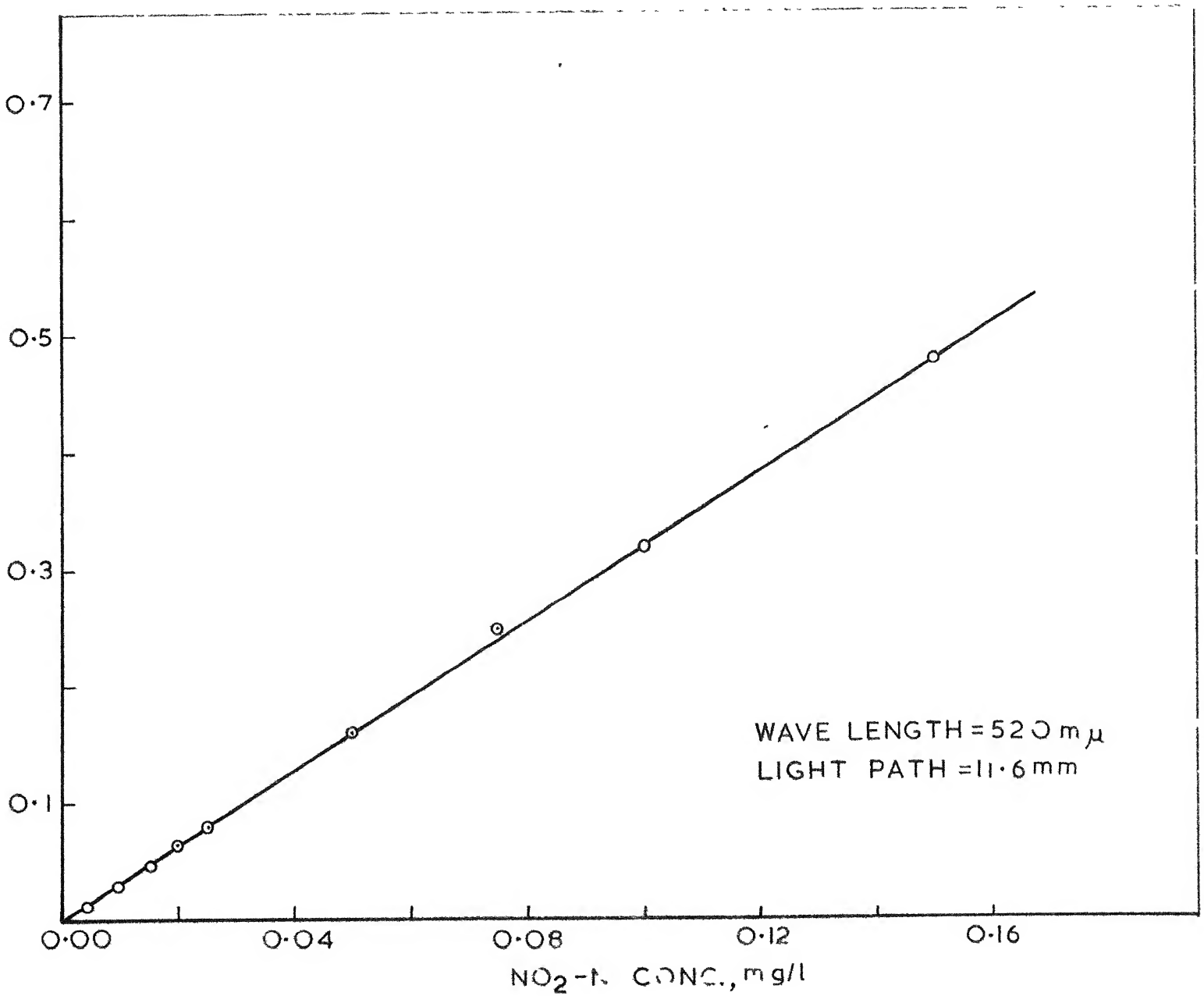


FIG. 7 IRVE FOR NO_2^-N

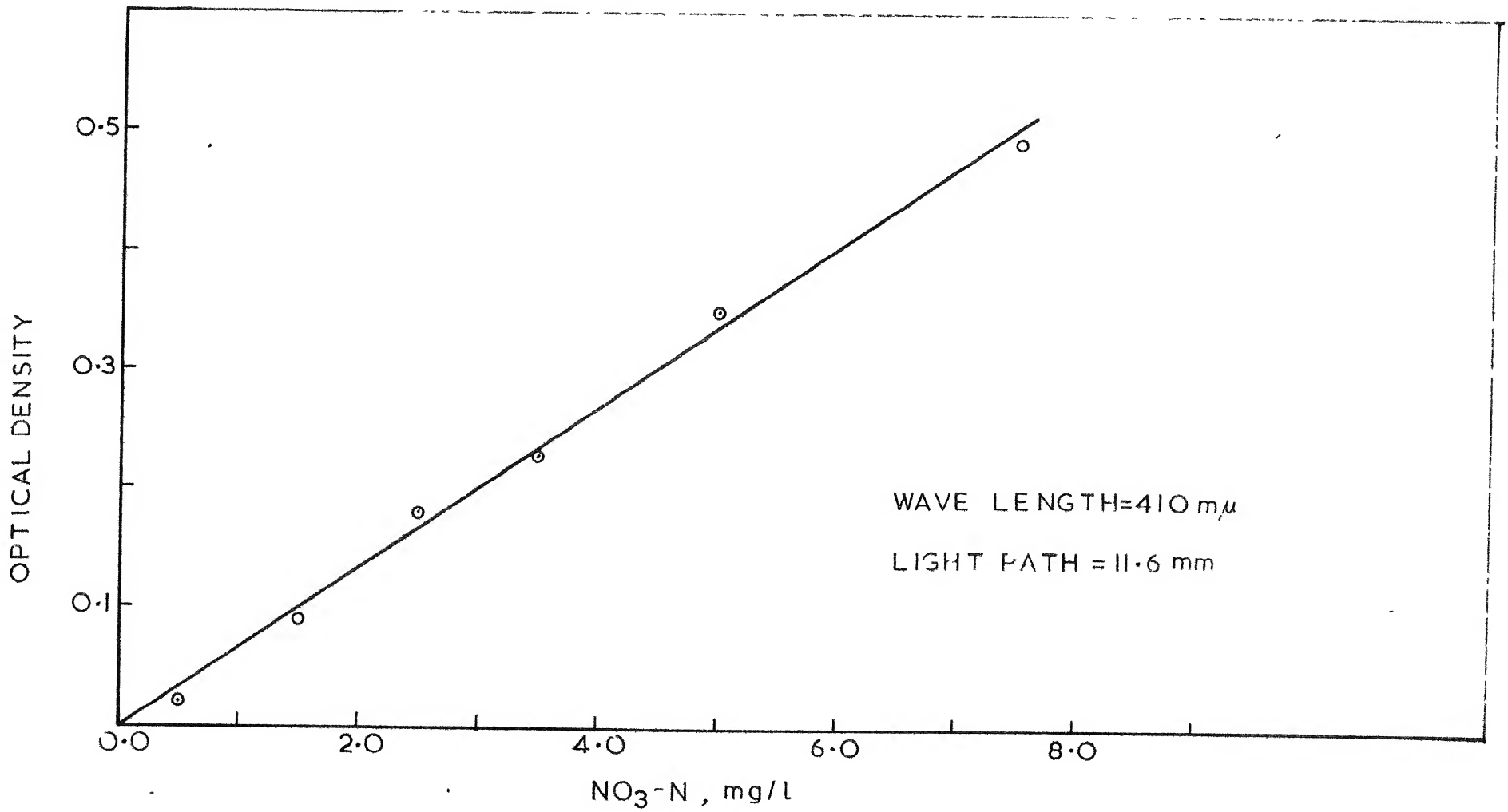


FIG 8 STANDARD CALIBRATION CURVE FOR NO_3-N

4. RESULTS AND DISCUSSION

4.1 Nitirification in a reactor with sand bed:

The nitrifying bacteria, as reviewed in Chapter 2 grow better if a supporting medium is provided to them. These bacteria stick to the surface of the supporting medium and multiply. Therefore for an efficient design of a nitrifying reactor a supporting medium should be provided. Two types of supporting media were investigated in this study, namely sand bed and packing straw. Further, since it is known that surface area available for growth plays a role in the rate of nitrification, the oxidation of Ammonia was observed for reactors having different surface area but having the same liquid volume of 5 liters. A reactor with no surface area for growth was also included. The NH_3-N concentration in the feed was kept at 750 mg/l. This concentration was chosen, because this may relate to actual effluent concentration of NH_3-N at various fertilizer plants. The pH was maintained as 8.0 through out the study.

Figures 9 and 10 show how nitrification proceeded in a reactor having 4 cms and 8 cms thickness of sand bed respectively with respect to time, when flow rates were varied. Since it was not known at what flow a wash out of organisms would occur, increasing flow rates as shown in figures 9 and 10 were tried.

It is seen from figure 9 that for 4 cm sand depth 92% nitrification occured at a flow rate of 1 l/day. The effluent contained about 82% NO_2-N and 10% NO_3-N of the total concentration of NH_3-N in the feed. On increasing the flow rate above 1.5 l/day

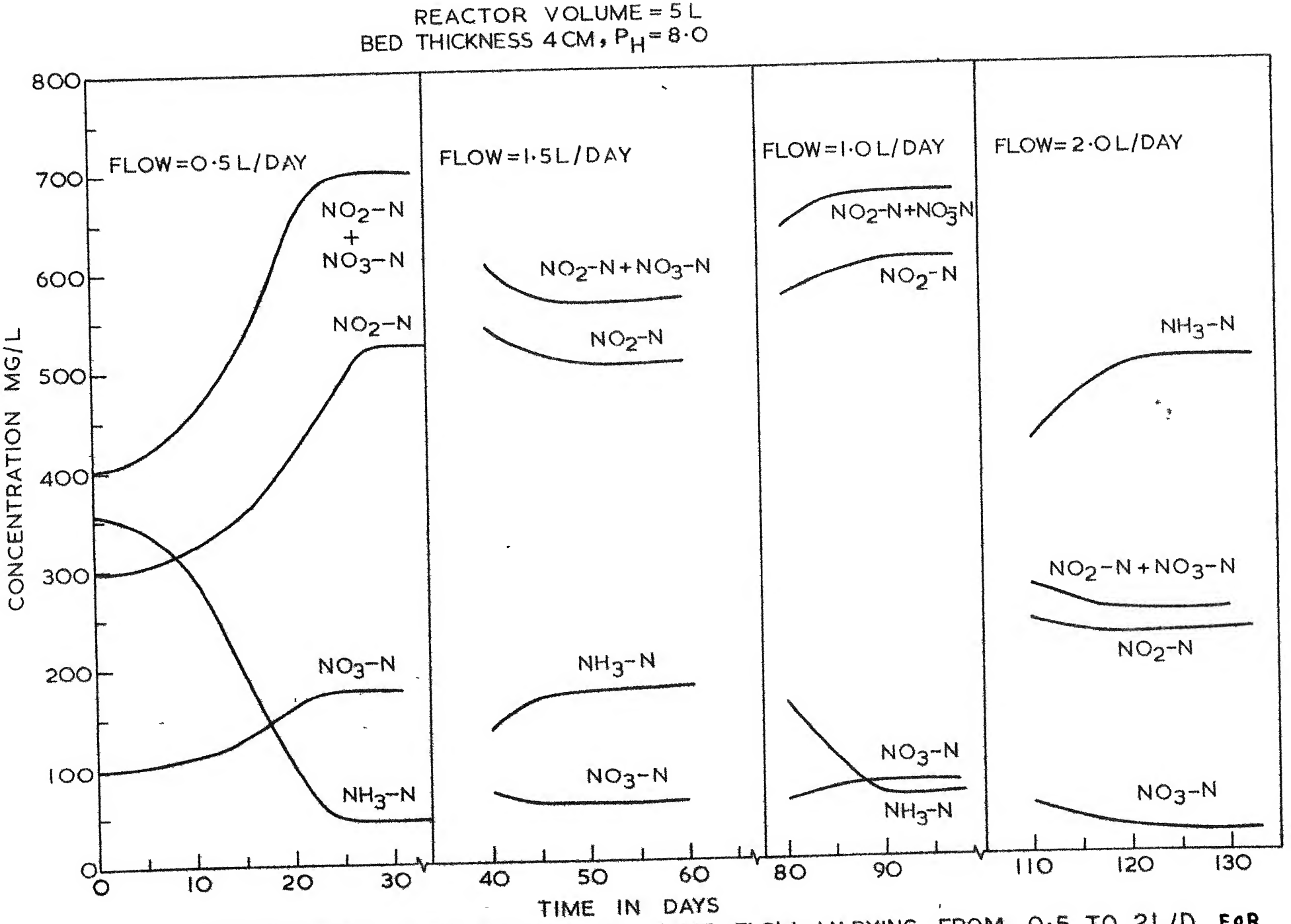


FIG. 9 NITRIFICATION WITH RESPECT TO TIME FLOW VARYING FROM 0·5 TO 2L/D FOR 4CM BED THICKNESS OF SAND.

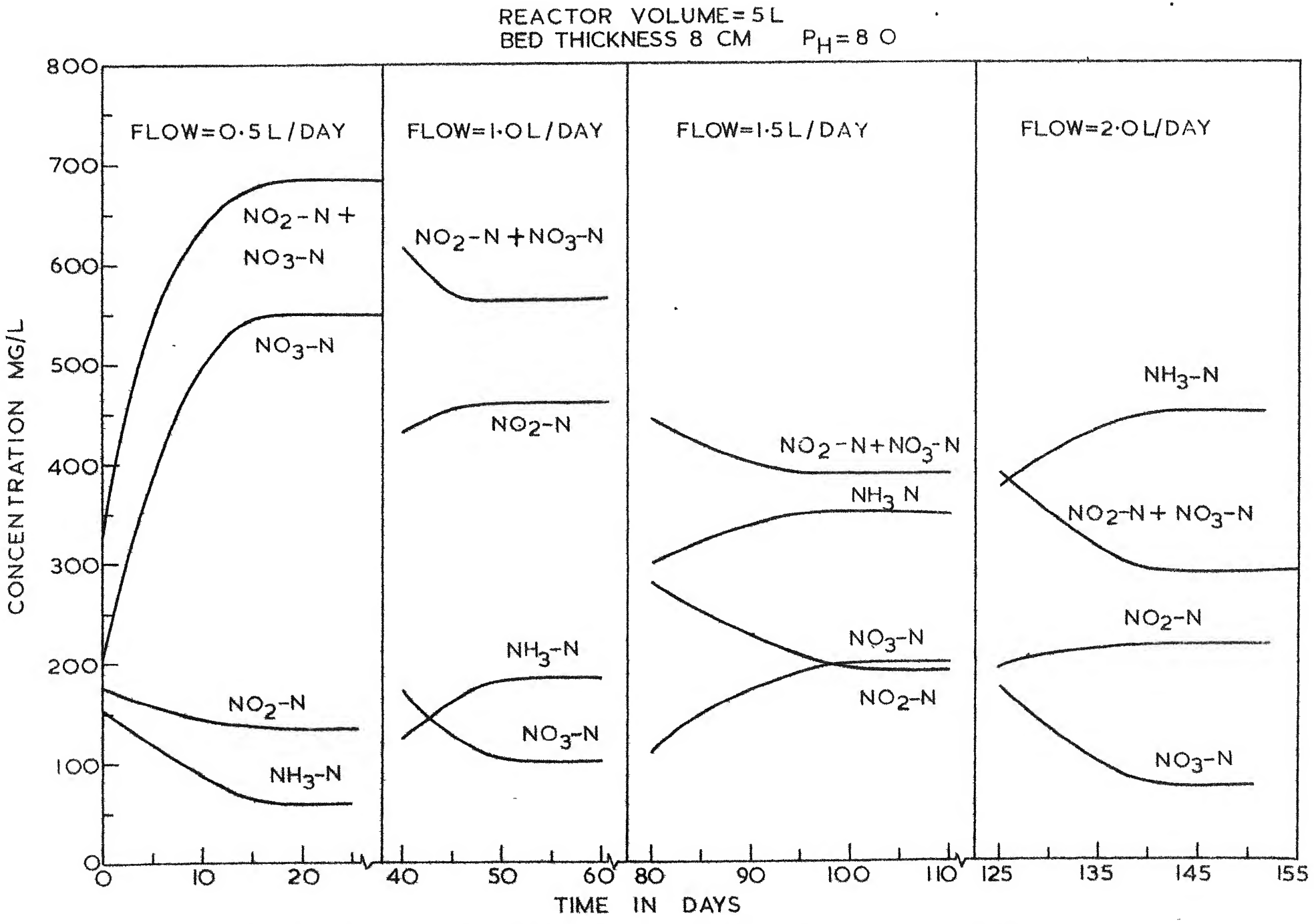


FIG. 10 NITRIFICATION WITH RESPECT TO TIME FLOW VARYING FROM 0·5L/D TO 2·0L/D FOR 8cm BED THICKNESS OF SAND.

the total nitrification was 77% and further increase in the flow rate to 2 liters/day, the nitrification reduced to only 33%. Such a flow rate for an influent concentration of NH_3-N as 750 mg/lit. would, therefore, not be suitable if complete nitrification is required.

From figure 10, it is seen that for 8 cm sand depth 92% nitrification occured at a flow rate of 0.5 l/day. The nitrification is less for higher flow rates. As the flow rates were increased to 1, 1.5 and 2 l/day the nitrification was 87%, 53% and 41% respectively. These observations therefore show a similar trend as shown by reactor having 4 cm deep sand bed.

The extent of total nitrification shown in figures 9 and 10 is also the total amount of nitrite formed since nitrite formation is an essential intermediate for NO_3-N formation. Here in this context it may be noted that during denitrification, NO_3-N is converted back to NO_2-N and therefore, reduction takes place. Since the proposed treatment process comprise of both nitrification and denitrification, nitrification may be continued only up to the oxidation of NH_3-N to NO_2-N and further oxidation of NO_2-N to NO_3-N is not necessary. Hence in present study the formation of NO_2-N only has been emphasized upon.

In order to find out the difference in nitrification for different surface area, the above data are plotted as shown in figure 11. The points in figure 11 have been plotted by considering the concentration of NH_3-N at equilibirium conditions for different flows against the dilution rate, D, which is given by the ratio of flow to reactor liquid velume. Since we are intrested in the removal of NH_3-N, the plot of fig. 11 has been made of NH_3-N concentration only.

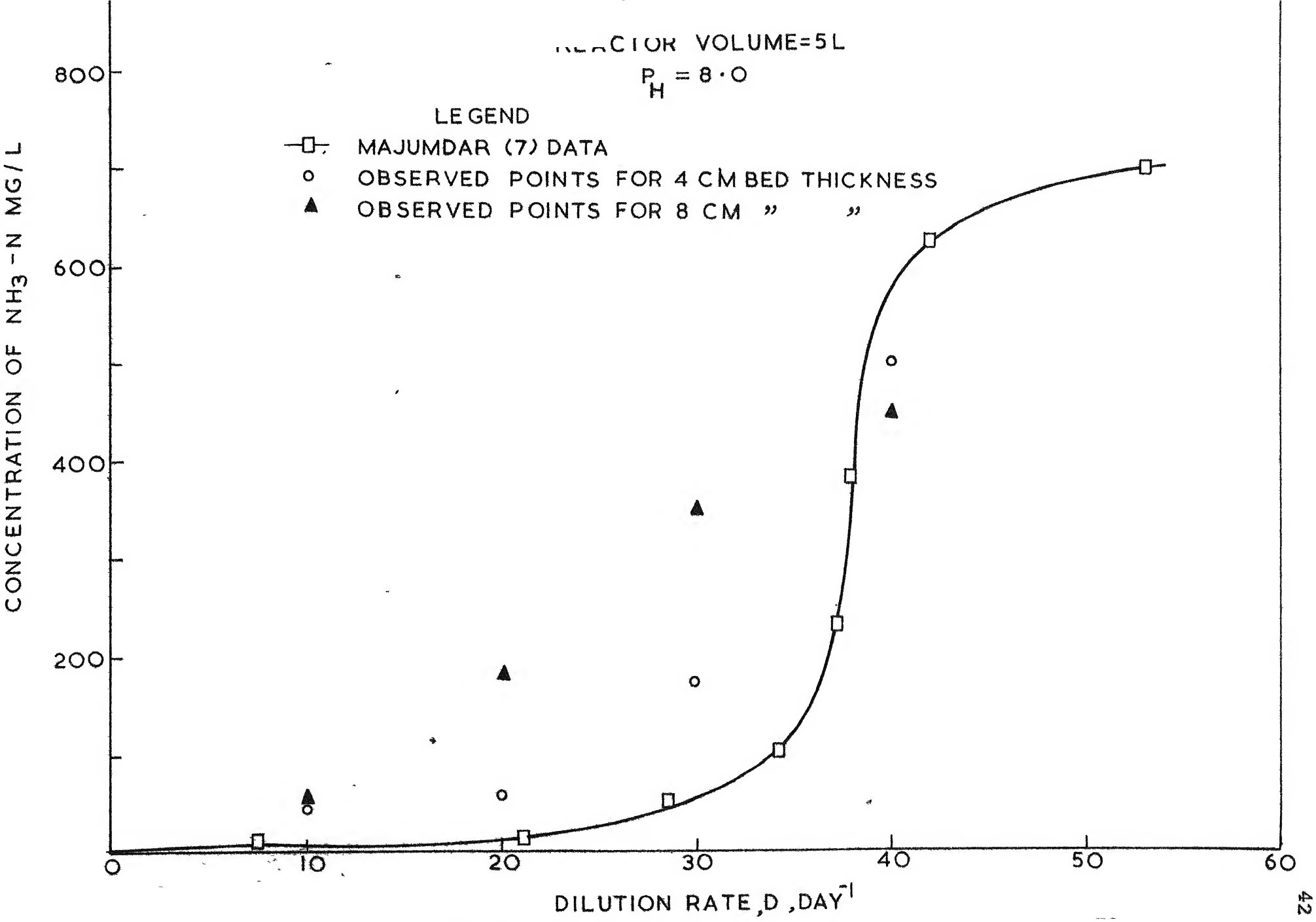


FIG. 11 EFFLUENT NH_3-N CONCENTRATION - DILUTION RATE RELATIONSHIP FOR A CONTINUOUS FLOW REACTOR WITH SAND

To compare the effect of surface area, the data obtained by Majumdar (7) are also shown in fig. 11. The depth of sand, gravel and glass beads for the reactor used by him was 1.0 cm. It is seen from this figure that nitrification is less for greater depth at lower flows, while the nitrification with varying depths is almost same for higher flows. Further for the dilution rate of 20 x 10^{-2} day^{-1} the NH_3-N concentration in the effluents are 60 and 200 mg/lit. for 4 cm and 8 cm bed thickness respectively while Majumdar (7) found this value as 10 mg/l. when the NH_3-H concentration in the feed was 700 mg/lit. From fig. 11, it is clear that there is significant difference in NH_3-N concentration for the three system up to a dilution rate of 30 x 10^{-2} day^{-1}. This may be due to the fact that the sand bed interfered with proper mixing in the reactor and the bacteria have not grown for full depth of the sand bed.

Since there was no improved nitrification for greater depth of sand bed, hence no further data were collected for higher dilution rates and no further study was carried out for greater thicknesses of sand bed.

4.2 Nitrification in reactor containing no bed:

Fig. 12 shows how nitrification proceeded with respect to time when flow rates were varied for a reactor with no supporting medium. Since it is not known which flow rate will be the best for design criteria an increasing order of flows as shown in fig. 12 was tried. The plot in fig. 12 shows the formation of total nitrite i.e. NO_2-N + NO_3-N for different flows.

From fig. 12, it is seen that at a flow rate of 0.5 l/day, 88% of total NH_3-N in the feed is converted to total nitrite i.e. NO_2-N + NO_3-N . As the flow rate increased, the nitrification

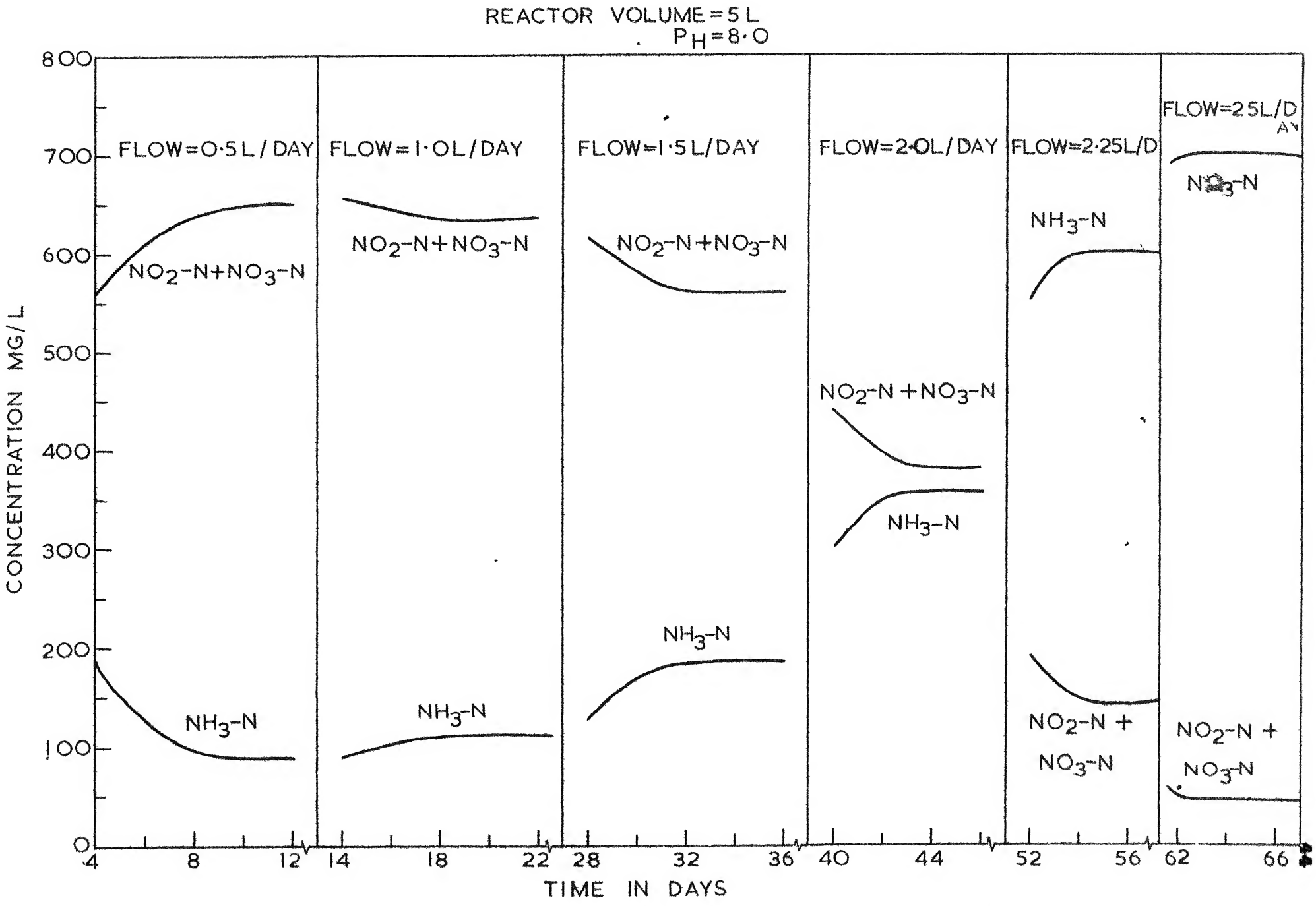


FIG. 12 NITRIFICATION WITH RESPECT TO TIME FLOW. VARYING FROM 0·5 TO 2·5L/D

decreased. At the flow rate of 2.5 lit/day the nitrification is only 17%.

The concentration of NH_3-N in the feed was 750 mg/lit. But from fig. 12 it is seen that the sum of total nitrogen i.e. NH_3-N + NO_2-N + NO_3-N in effluent for different flows varies from 730 to 745 mg/lit. This difference is probably due to the fact that some of the nitrogen will be used up in building the cell protoplasm and some error in estimation.

From this study the value of maximum specific growth rate (μ_{max}) and saturation constant (K_s) can be calculated out. Aiba et al (39) have stated that under steady state condition the specific growth rate (μ) is equal to dilution rate, D. This they have achieved by considering a mass balance of micro-organism at equilibirium conditions as shown below -

Change with in the reactor = Influent + growth - effluent

$$V \frac{dX_1}{dt} = FX_o + \mu X_1 V - FX_1 \qquad \ldots \quad (12)$$

where V = reactor volume

F = flow rate, volume/time

X_o = organism concentration in influent, mass/volume

X_1 = organism concentration in effluent, mass/volume

If we assume that there are no organisms in the influent and recognize that the hydraulic residence time, $\theta = V/F$, equation 12 can be rearranged.

$$\frac{dX_1}{dt} = (\mu - \frac{1}{\theta}) X_1 \qquad \ldots \quad 13$$

at steady state $\frac{dX_1}{dt} = 0$,

$$\mu = \frac{1}{\theta} = D \quad \ldots \quad \ldots \quad 14$$

Further Monod has shown that the value of specific growth rate can be given as

$$\mu = \frac{\mu_{max}\, S_1}{K_s + S_1} \quad \ldots \quad \ldots \quad 9$$

Equation 9 can be rearranged as

$$\frac{1}{\mu} = \frac{K_s}{\mu_{max}} \frac{1}{S_1} + \frac{1}{\mu_{max}} \quad \ldots \quad \ldots \quad 15$$

Therefore when $1/\mu$ i.e. detention time is plotted against the reciprocal of the substrate concentration in the effluent a linear plot is obtained. Such a plot of the experimental data is given in figure 13. The slope of line is equal to K_s/μ_{max} and the ordinate intercept is $1/\mu_{max}$. From analysis of these data the saturation constant K_s was found to be 238 mg/l and maximum specific growth rate, μ_{max}, as 0.667 day^{-1}.

The value of μ_{max} is quite comparable with the values obtained by other worker for batch cultures. Buswell et al (35) found this value increasing from 0.5 day^{-1} to 2 day^{-1} for temperature variation of 15°C to 32°C. At 23°C, the average maintained in this study the value was 0.667 day^{-1}. Painter and Loveless (35) obtained this value as 0.7 to 0.9 day^{-1} at 25°C for batch cultures. Thus we see that the value of μ_{max} is quite comparable. However, the maximum growth rate is known to vary with the operating conditions, types of substrate and type of culture. The variation in values obtained in this study may be due to different operating condition.

Fig. 14 shows the observed change in NH_3-N concentration with dilution rate and also a theortical plot obtained by using the values of K_s and μ_{max} obtained.

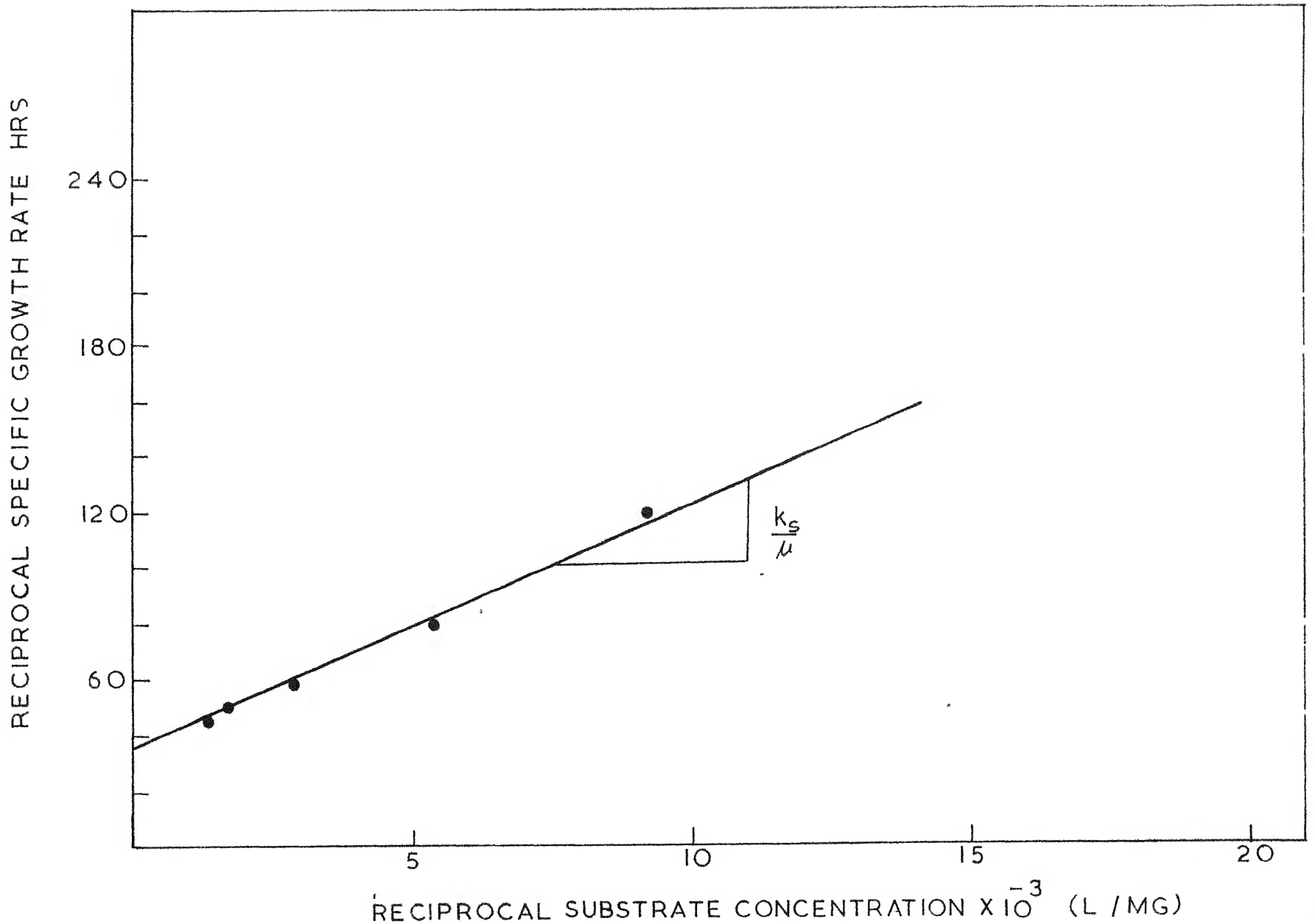


FIG 13 BIOLOGICAL CONSTANT WERE DETERMINED BY PLOTING SPECIFIC GROWTH RATE RECIPROCAL VS SUBSTRATE CONCENTRATION RECIPROCAL

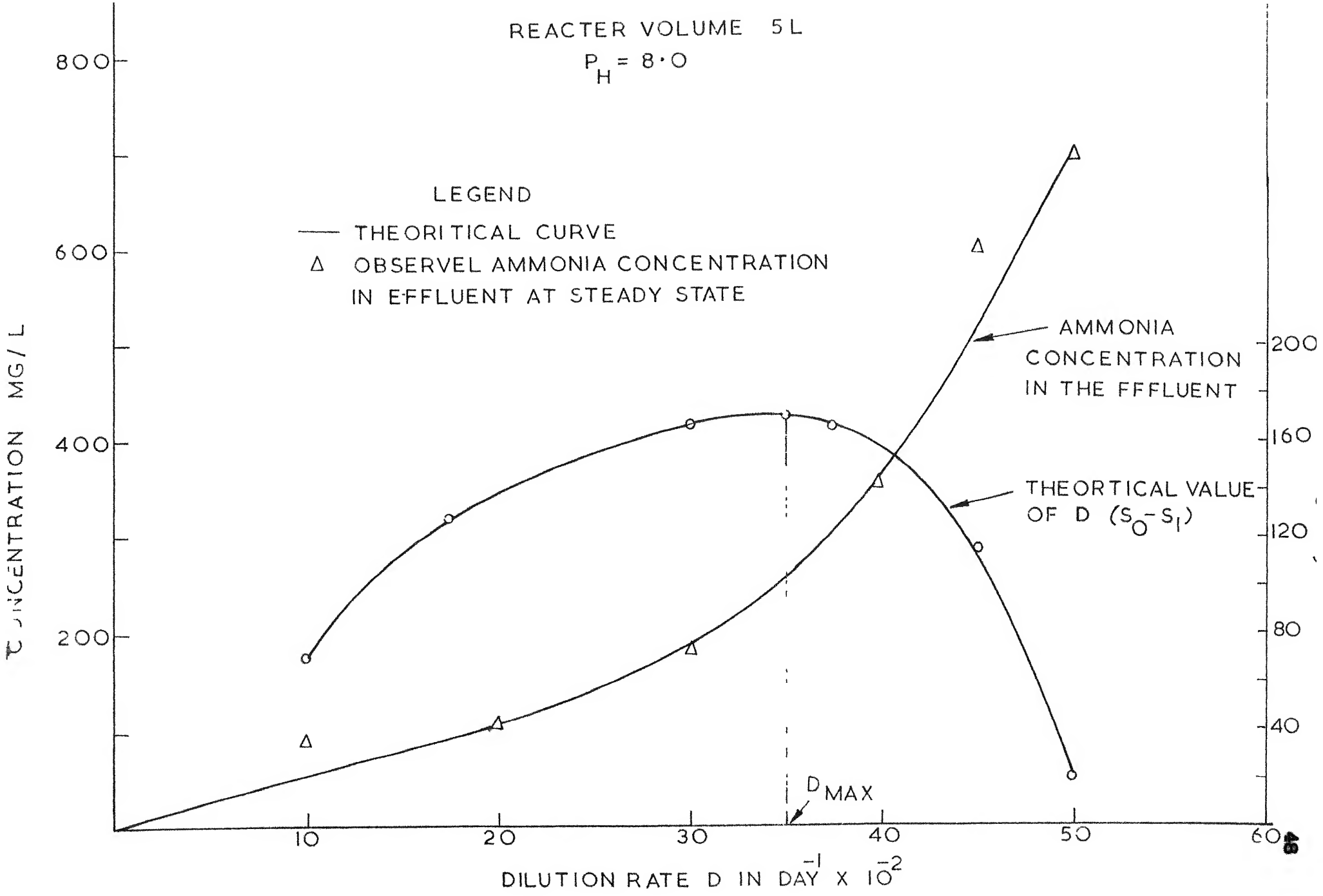


FIG 14 THEORTICAL AND OBSERVED CHANGE IN NH_3-N CONCENTRATION AND MAXIMUM NITRIFICATION/UNIT VOLUME WITH RESPECT TO DILUTION RATE FOR A REACTOR HAVING NO SUPPORTING MEDIUM

The theortical curve has been plotted by using the equation

$$\mu = \frac{u_{max}\, S_1}{K_s + S_1} \quad \ldots \quad \ldots \quad 9$$

or $$S_1 = \frac{K_s . D}{\mu_{max} - D} \quad \ldots \quad \ldots \quad 16$$

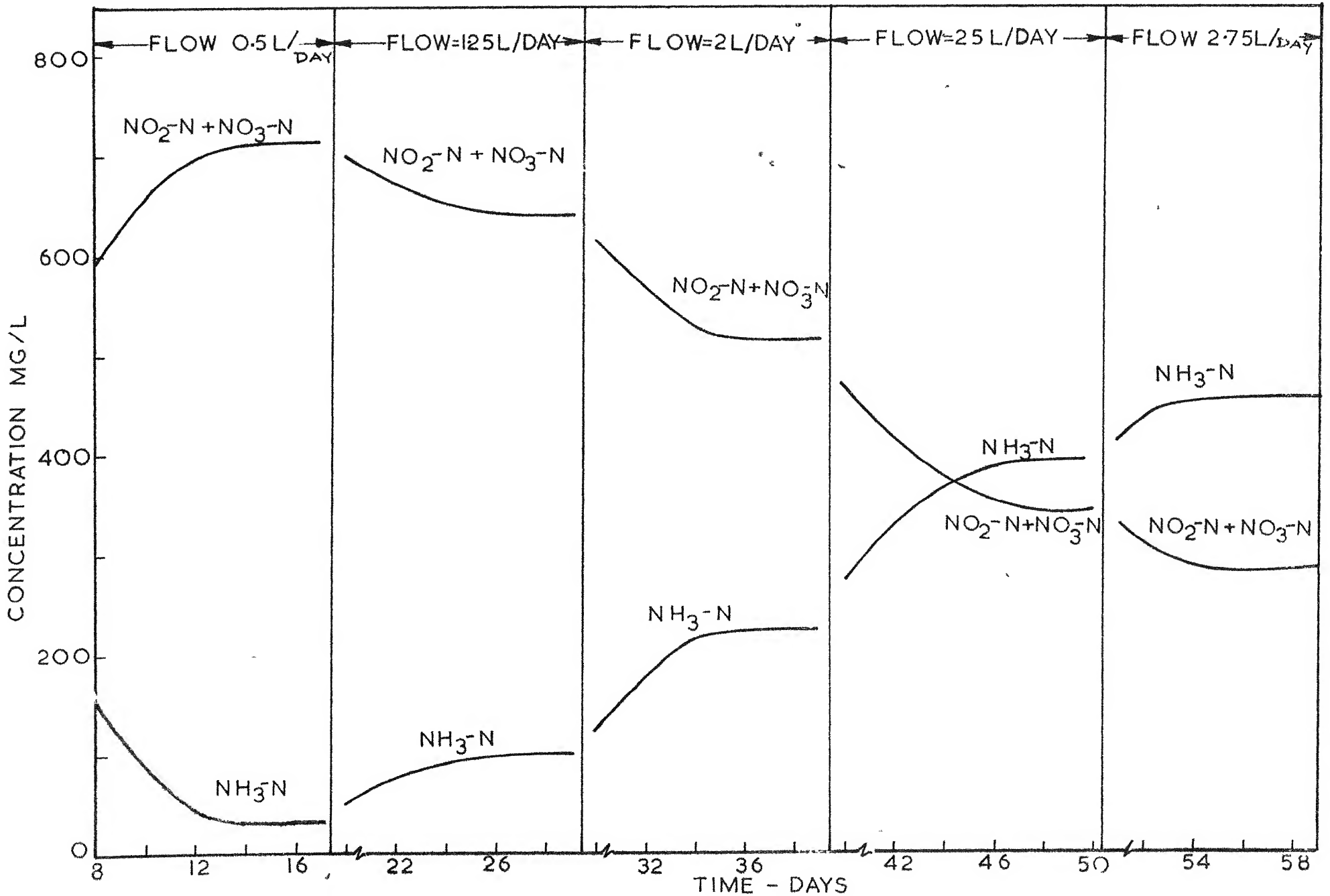
Since there is a fairly good agreement between the theortical and observed values it can be concluded tha t the fitted line in figure 13 was appropriate and the system behaves according to the theortical postulation by Monod and others (39).

Fig. 14 also shows the plot between dilution rate, D, and theortical values of D ($S_o - S_1$), such a plot will give the critical flow for the maximum nitrification/unit volume. From the figure it is seen that initially the value of $D(S_o - S_1)$ increases with the increase in the value of D and then it starts decreasing with the further increase in value of D. From this figure it is clear that the value of 35×10^{-2} day^{-1} for D will give the maximum value of D ($S_o - S_1$). Hence in designing the reacter the value of D should be taken nearly 35×10^{-2} day^{-1} for maximum removal of NH_3-N. However, if there is a limit imposed on the maximum concentration of NH_3-N going out, the value of D will be decided by this consideration.

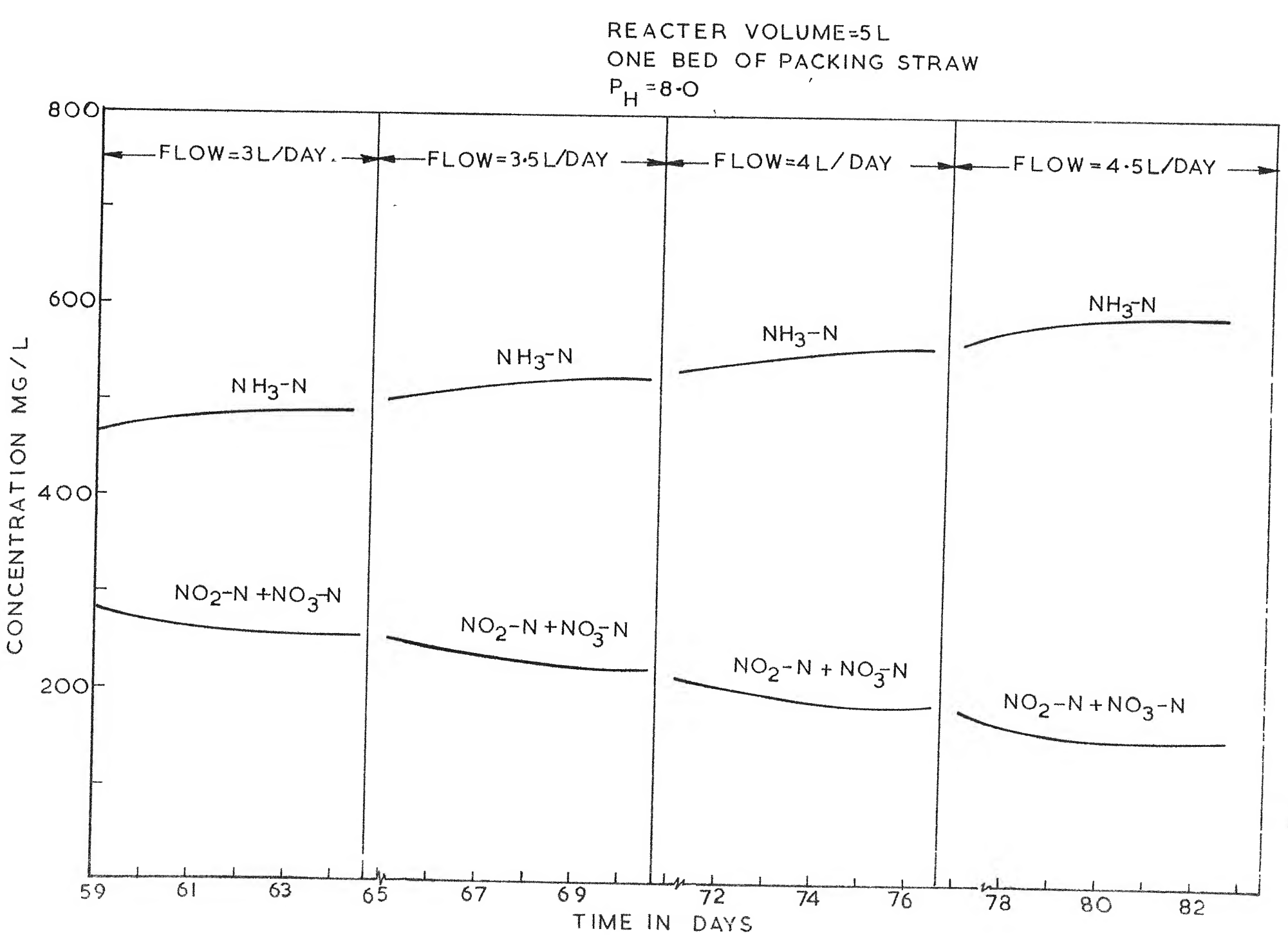
4.3 Nitrification in a reactor having packing straw as a supporting medium:

Figures 15 to 18 show how nitrification proceeded with respect to time in a reactor having one and two supporting beds of packing straw, when flows were varried. Each bed of straw provided a surface area of about 1860 sq.cm. When 10 gms of packing straw was used in thin layer between folded wire gauze.

REACTOR VOLUME = 5 L
ONE BED OF PACKING STRAW
P_H = 8 0



TRIFICATION WITH RESPECT TO TIME WHEN FLOW RATE VARIES FROM 0·5 L/DAY



NITRIFICATION WITH RESPECT TO TIME WHEN FLOW VARYING FROM 3L/DAY TO 4·5L/DAY

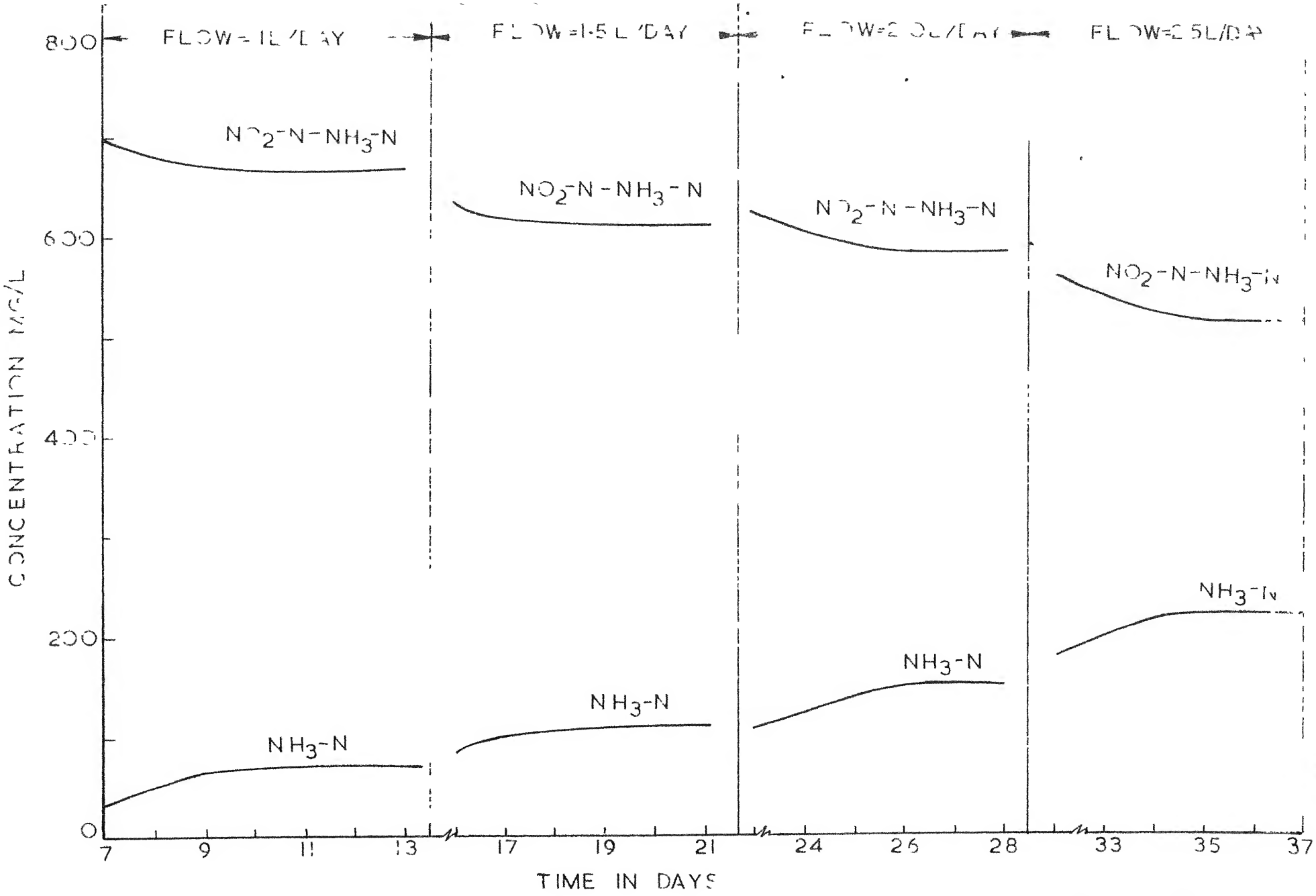


FIG. 17 NITRIFICATION WITH RESPECT TO TIME WHEN FLOW VARYING FROM 1L/DAY TO 2·5L/DAY

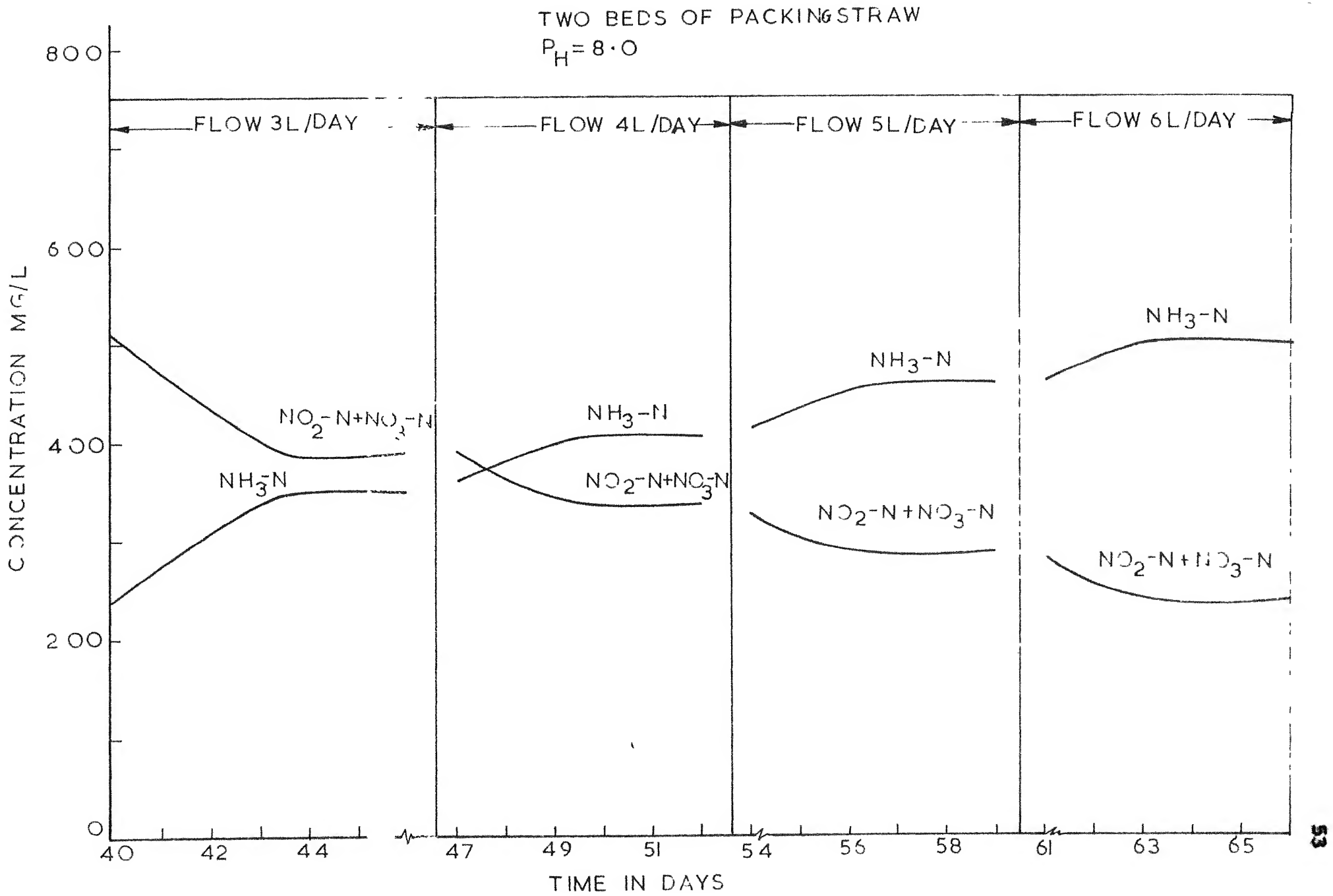


FIG.18 NITRIFICATION WITH RESPECT TO TIME WHEN FLOW VARYING FROM 3·5L/DAY TO 6L/DAY

From figures 15 and 16 for one bed, it is seen that at a flow of 0.5 l/day nitrification is almost 100% complete and it decreases as the flow rate increases. The decrease in percent nitrification is more in the lower ranges of flow as compared to higher range offlow. The nitrification decreases from 98% to 47% for the flow variation of 0.5 l/day to 2.5 l/day. While for the flow variation of 2.75 l/day to 4.5 l/day the reduction in nitrification is only from 35% to 20%.

Similarly for two bed systems as seen from figures 17 and 18 that at a flow of 1 l/day the nitrification is 91% and it decreases as the flow rate increases. But in this case the nitrification decreases from 91% to 50% for the flow variation of 1 l/day to 3 l/day and from 50% to 33% for the variation of 3 l/day to 6 l/day.

The curves in figure 19 have been plotted by considering the concentration of NH_3-N at equilibirium condition against the dilution rate. It also shows the data for the reactor without any bed. From figure 19, it is seen that there is less difference in NH_3-N concentration for all the systems at lower flows i.e. up to a dilution rate of 25×10^{-2} day^{-1}, while there is significant difference at higher dilution rates. In the reactor having no supporting medium, there is a significant difference in NH_3-N concentration for the change of dilution rate from 30×10^{-2} day^{-1} to 45.0×10^{-2} day^{-1}. Since the amount of substrate removed depends on the mass of active organism present in the system, it is clear that for change in dilution rate from 30×10^{-2} day^{-1} to 45×10^{-2} day^{-1} greater mass of organisms are washed out from this reactor and there is a complete wash out when growth rate can no longer keep up with dilution rate.

In case of reactor with supporting bed, we see that there is significant removal of NH_3-N at even 50 x 10^{-2} day^{-1} and the removal in the two bed system is more than the single bed system. This is because bacteria are sticking to the bed and, therefore, they can not be washed out. In two bed system, a greater mass of organisms can get attached to the bed and therefore, the removal in this system will be more.

It is seen from curve II and III of fig. 19 that substrate concentration approches to a constant value as the dilution rate increases. This shows that there will be a constant removal by the attached organisms for higher dilution rates.

Kornegay and Andrews (36) have suggested the following equation as reveiwed earlier in chapter 2 on the assumption that substrate utilization due to source other then the attached film is small and may be neglected.

$$F(S_o - S_1) = \frac{\mu_{max}\, S_1}{K_s + S_1} \quad \frac{(A)(X)(d)}{Y} \quad \ldots \quad \ldots \quad 10$$

where μ_{max} = maximum specific growth rate,

K_s = saturation constant

A = Surface area of supporting media

X = organism concentration

d = thickness of film.

They verified the above proposed equation for the high flow of influent in the reactor i.e. for low residence time. They found that at residence times of less than 7.5 min. the suspended organisms were washed out and any nutrient utilization due to small quaintity of micro-organism being washed from walls was negligible.

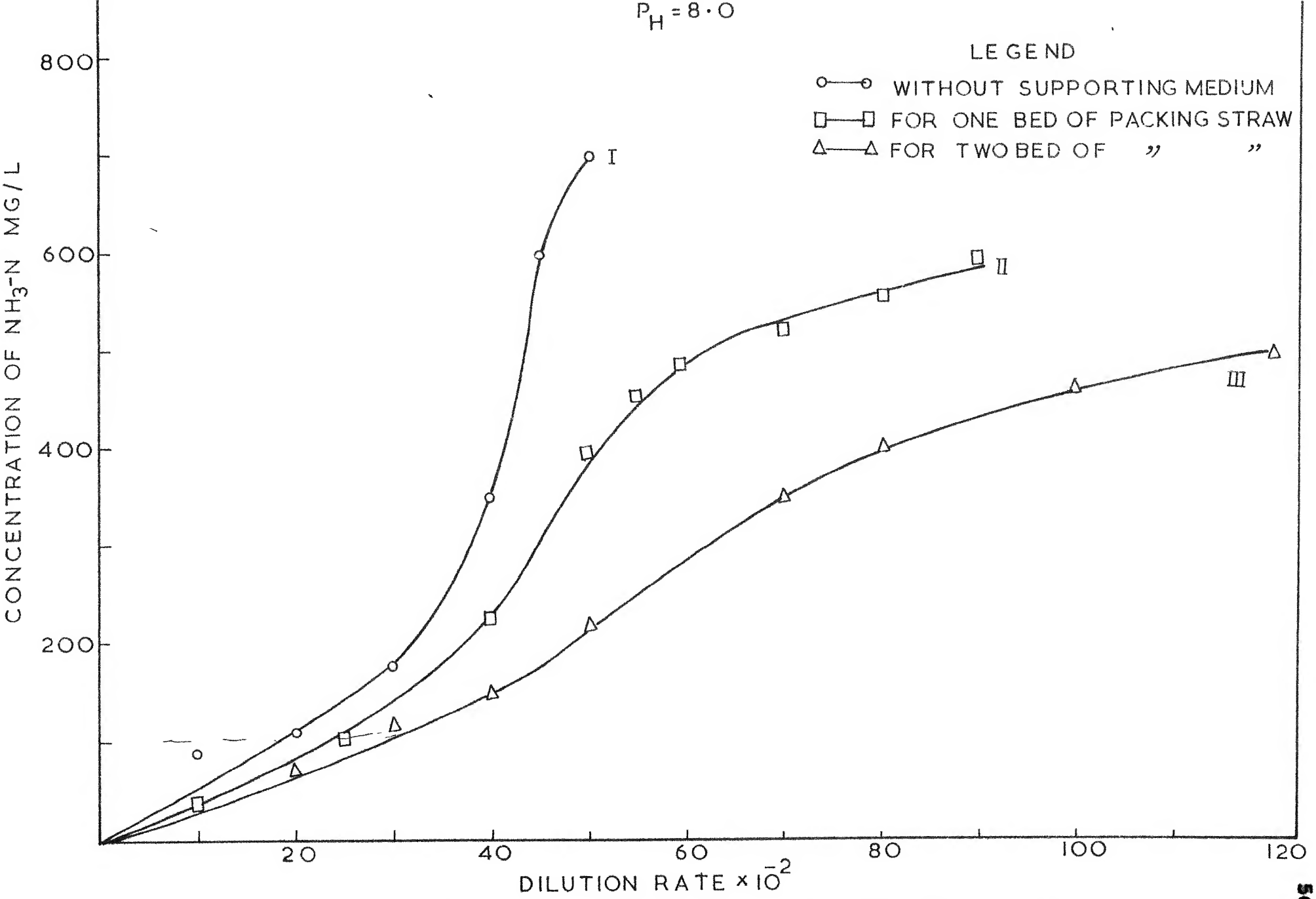


FIG 19 RATE OF NITRIFICATION IN A CONTINOUS FLOW REACTER WITH & WITHOUT SUPPORTING MEDIUM

Kornegay and Andrews (36) also found from their studies that during the transition period of film accumulation the thickness of film was increased and eventually reached a constant thickness and greater film thickness resulted in no increase in the rate of removal. This shows that the active mass of organisms attached to the bed reaches to a constant value. This constant mass of organism attached to the bed can be found out by the following equation which can be obtained by rearranging the equation 10.

$$\frac{(A)(X)(d)}{Y} = \frac{F(S_o - S_1)}{\mu_{max} S_1} (K_s + S_1) \quad \ldots \quad 17$$

For finding the theortical substrate concentration (S_1) in effluent the equation 17 can be rearranged as follows:

$$S_1 = \frac{-\left[\frac{(A)(X)(d)}{Y \cdot F}\mu_{max} + K_s - S_o\right] + \sqrt{\left(\frac{(A)(X)(d)}{Y F}\mu_{max} + K_s - S_o\right)^2 + 4K_s \cdot S_o}}{2} \quad \ldots \quad \ldots \quad 18$$

As the present study has been carried out for low flows also the above mentioned equation can not be applied to all data's. The removal of substrate at lower flows will be both by the suspended organisms and organisms attached to the bed, since at lower flows suspended organisms will not be washed out. In such a case, equations suggested by Kornegay and Andrews (36) are not applicable. For such a system, different set of equations can be derived as follows.

The substrate balance for such system can be as

Change = Input - out put - utilization of substrate by organism on bed - utilization by organism in suspension.

$$\left(\frac{dM_s}{dt}\right)_{net} = FS_o - FS_1 - \left(\frac{dM_s}{dt}\right)_{\substack{\text{utilization} \\ \text{on bed.}}} - \left(\frac{dM_s}{dt}\right)_{\substack{\text{utilization in} \\ \text{suspention}}} \quad \ldots \quad 19$$

S_o - Influent substrate concenstration

F - flow rate

Monod showed that substrate utilization and the corresponding organism growth may be related by the expression

$$\left(\frac{dM_s}{dt}\right)_{growth} = \frac{1}{y}\left(\frac{dM_o}{dt}\right)_{growth}$$

where y = yield constration

The rate of change in the mass of organisms may be written as the product of specific growth rate constant and the mass of organism i.e.

$$\left(\frac{dM_o}{dt}\right)_{growth} = \mu M_o$$

So equation 19 reduces to

$$\left(\frac{dM_s}{dt}\right)_{net} = FS_o - FS_1 - \frac{\mu}{y}(Mo)_{on\ bed} - \frac{\mu}{y}(Mo)_{in\ suspention} \quad \ldots 20$$

$$(Mo)_{bed} = (A)(X)(d) \quad \ldots \quad \ldots 21$$

$$(Mo)_{suspention} = X_1 V \quad \ldots \quad \ldots 22$$

where X_1 is organism concentration in effluent (Mass/Volume)

From equations 20,21 and 22 the following equation can be obtained

$$\left(\frac{dM_s}{dt}\right)_{net} = FS_o - FS_1 - \frac{\mu}{y}(A)(X)(d) - \frac{\mu}{y} X_1 V \quad \ldots 23$$

At steady state $\left(\frac{dM_s}{dt}\right)_{net} = 0$ and $X_1 = y(S_o - S_1)$

Equation 23 reduces to

$$F(S_o - S_1) = \frac{u}{y}(A)(X)(d) + \mu (S_o - S_1)V$$

$$= u\left[\frac{(A)(X)(d)}{Y} + (S_o - S_1)V\right]$$

$$\text{or } \frac{1}{\mu} = \frac{(A)(X)(d)/y + (S_o - S_1)V}{F(S_o - S_1)} \quad \ldots \quad 24$$

From Monod expression the value of μ can be given as

$$\mu = \frac{\mu_{max}\, S_1}{K_s + S_1} \quad \ldots \quad \ldots \quad 9$$

Hence the equation 20 reduces to

$$\frac{K_s + S_1}{\mu_{max}\, S_1} = \frac{(A)(X)(d)/y + (S_o - S_1)V}{F(S_o - S_1)} \quad \ldots \quad 25$$

The theortical value of S_1 can be find out by equation 25 which can be rearranged as follows.

$$S_1 = \frac{-\left[F(S_o - K_s) - \mu_{max}\left\{\frac{AXd}{y} + S_o V\right\}\right] \pm \sqrt{\left[F(S_o - K_s) - \mu_{max}\left\{\frac{AXd}{y} + S_o V\right\}\right]^2 - \left[4(V\mu_{max} - F)(K_s S_o F)\right]}}{2\left[V\ \mu_{max} - F\right]}$$

.... 26

From fig. 19 it is seen that the significant removal of substrate by the organisms in suspension only is up to a dilution rate of 50 x 10^{-2} day^{-1} and beyond this dilution rate wash out occured. Hence in a reactor having supporting medium, the substrate removal at lower flows is by organism both which are in suspension and those attached to the bed, ahd the substrate removal at higher flows is only by organisms attached to the bed.

Curve I of fig. 19 shows that the organism remains in suspension up to a dilution rate of 50 x 10^{-2} day^{-1}. Hence a reactor having supporting medium will have organisms in suspension up to a dilution rate of 50 x 10^{-2} day^{-1} and beyond this dilution rate organism attached to the bed will be active and the mass of organisms will be constant. For such dilution rates the system will be same as proposed by Kornegay and Andrews (36). The constant mass of organisms attached to the bed is calculated for different dilution rates, by using the equation 17 for both the reactors having one bed and two beds. These values are shown in fig. 20. In calculating the values of AXd/y the μ_{max} and K_s are taken as

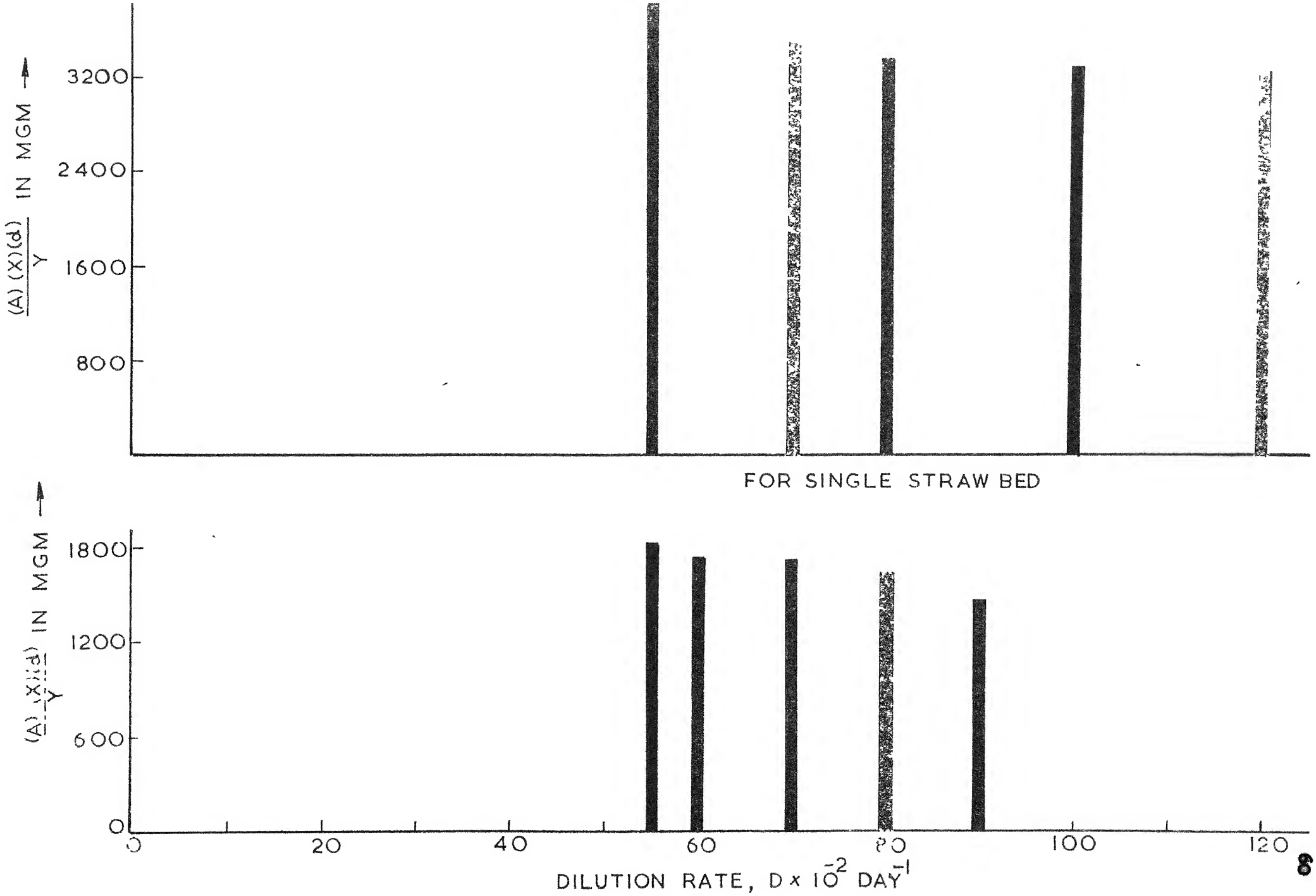


FIG 20 GRAPH SHOWING VARIATION OF AXd/y WITH DILUTION RATE FOR SINGLE AND DOUBLE STRAW BEDS

0.667 day^{-1} and 238 mg/lit. From fig. 20, it is seen that the value of $\frac{AXd}{y}$ is almost same for all the dilution rate. For finding the mass of organism attached to the beds, the average of value of (A)(X)(d)/y is taken.

The mean value of (A)(X)(d)/y for a single bed system comes out to be 1675 mg and for two bed it is 3400 mg. The surface area provided in both the reactor are 1860 sq.cm. and 3720 sq.cm. respectively. If we assume the value of y as 0.05 the concentration of organism on the supporting medium for single bed system is 0.045 mg/sq.cm and two bed system is 0.0457 mg/sq.cm. The values of micro-organisms concentration on supporting medium in both the system is almost same, this shows that the mass of organisms attached on two beds is double of that of mass attached on single bed.

Fig. 21 shows the theortical curve and observed change in NH_3-N concentration with dilution rate. Theortical curve is plotted by using the equation 18 and 26. Equation 18 is used for finding the theortical values of NH_3-N concentration in effluent for dilution rates more than 50 x 10^{-2} day^{-1} and equation 26 is used for dilution rate 50 x 10^{-2} day^{-1} and less. In both the cases the values of AXd/y, K_s and u_{max} are taken as 1675 mg, 238 mg/l and 0.667 day^{-1}.

Fig. 22 shows the theortical curve and observed change in NH_3-N concentration with dilution rate for two bed system. The theortical values have been calculated by similar manner as in the case of single bed system. In this case mass of organisms attached to the bed will be double of that of for single bed. In calculating the theortical curve the value of (A)(X)(d)/y is

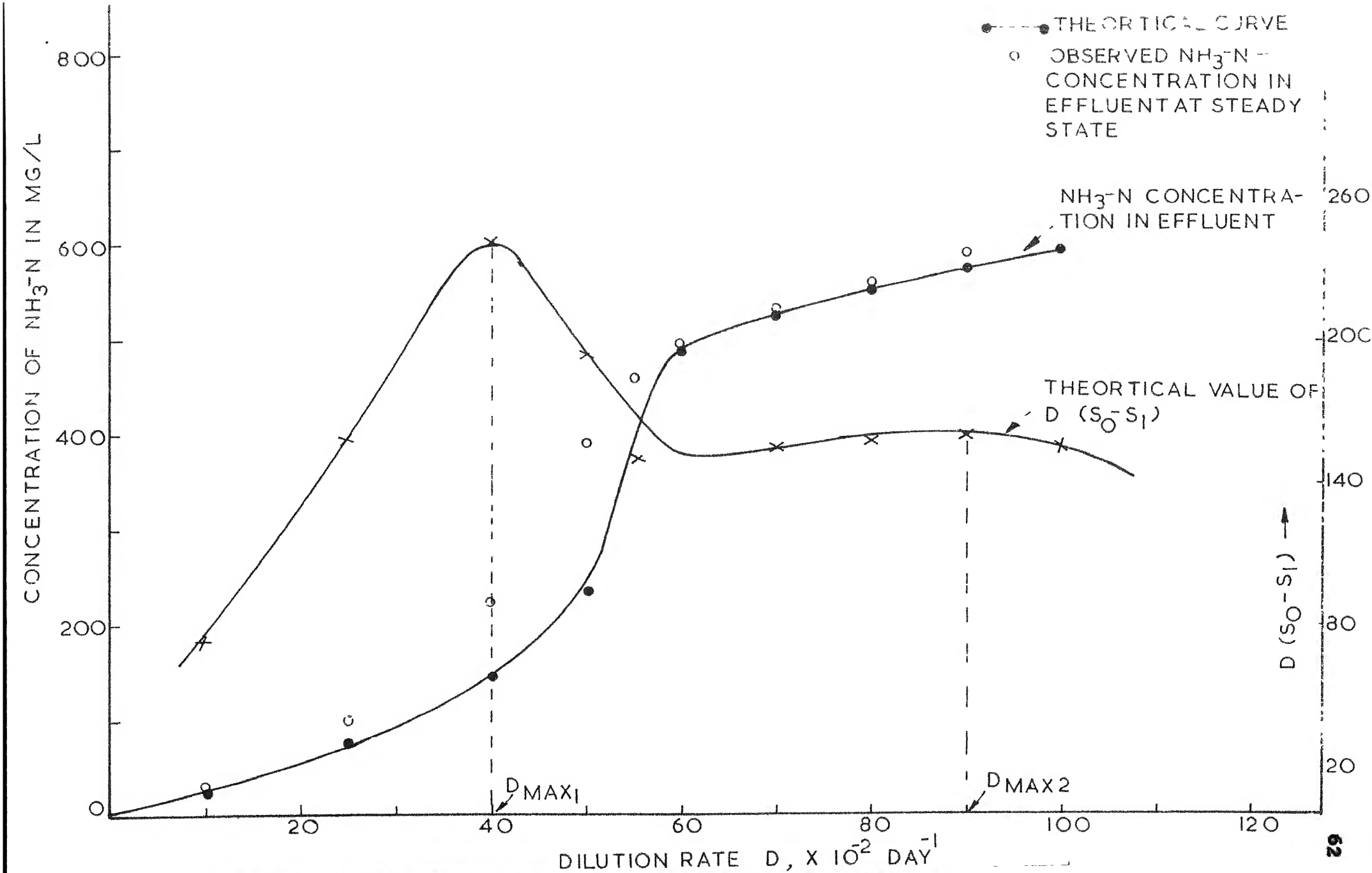


FIG 21 THEORTICAL AND OBSERVED NH_3-N CONCENTRATION IN THE EFFLUENT AND MAXIMUM NITRIFICATION/UNIT VOLUME WITH RESPECT TO DILUTION RATE FOR AS CONTINUOUS FLOW REACTOR WITH SINGLE STRAW BED

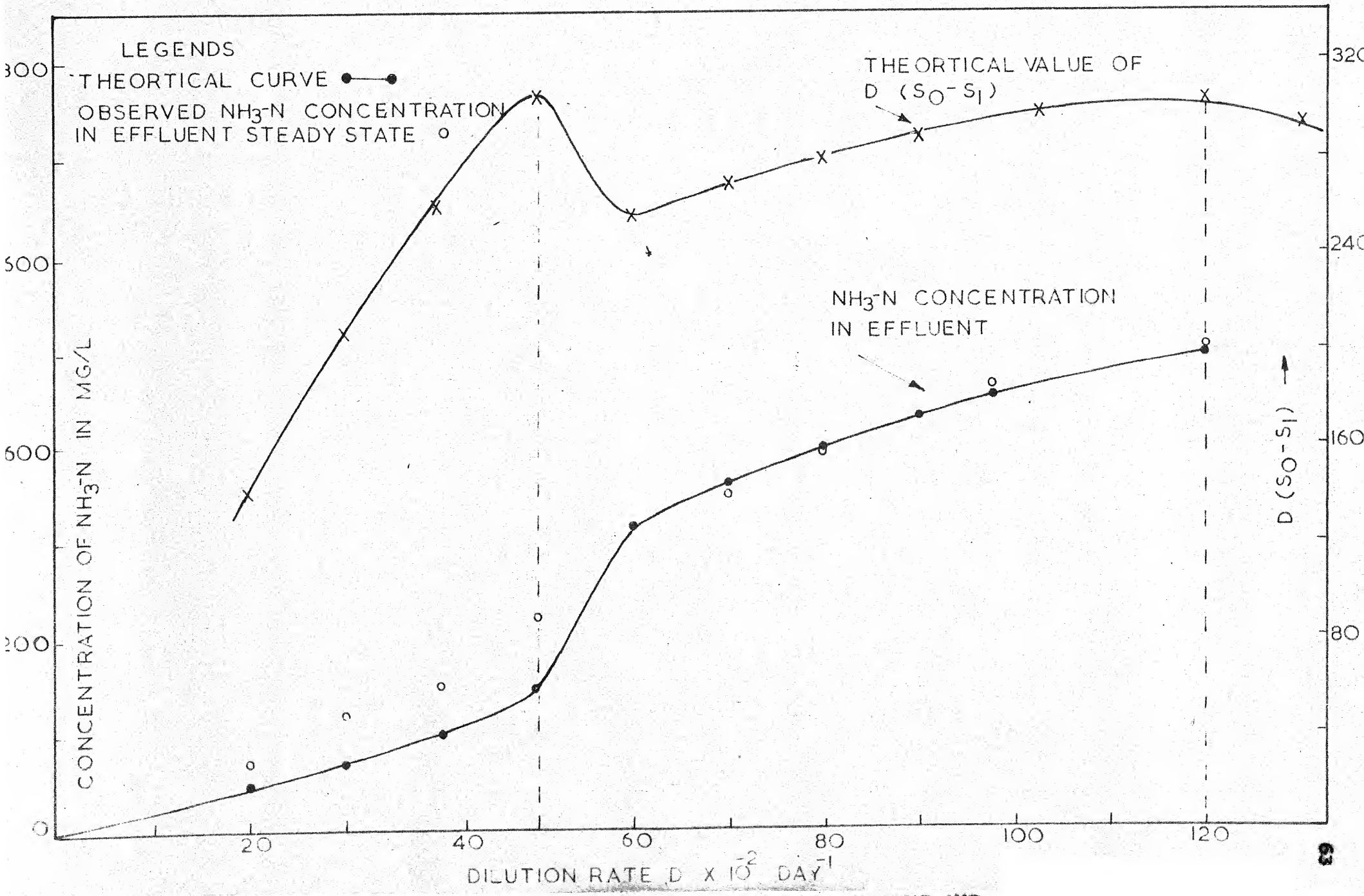


FIG 22 THEORTICAL AND OBSERVED NH_3-N CONCENTRATION IN THE EFFLUENT AND MAXIMUM NITRIFICATION/UNIT VOLUME WITH RESPECT TO DILUTION RATE FOR A CONTINOUS FLOW REACTOR WITH TWO STRAW BEDS

taken as 3350 mg, and the values of K_s and μ_{max} as 238 mg/l and 0.667 day^{-1}.

The following facts can be noted from an examination of fig. 21 and 22.

(a) The effluent substrate concentration approaches a constant value as the dilution rate is increased.

(b) There is a close agreement between theortical curve and observed results which support the validity of the model proposed by Kornegay and Andrews (36) for this system.

(c) There is a sudden rise in NH_3-N concentration for the change in dilution rate from 50 x 10^{-2} to 60 x 10^{-2} day^{-1} for both the system i.e. single and double bed systems. This shows that all the organisms in suspension have been washed out during this variation of dilution rate.

Different influent concentrations of NH_3-N were not tried, but on theortical basis it can be said that the effluent concentration will not be independent of the influent concentration as in the case of completely mixed slurry reactor system.

Fig. 21 and 22 also show the plot between dilution rate and the calculated $D(S_o-S_1)$ as it was made for system having no supporting medium. Here for both the system we have got two peak values of D. For the single bed the value of D are 40 x 10^{-2} day^{-1} and 90 x 10^{-2} day^{-1} while for two bed system the values are 50 x 10^{-2} day^{-1} and 120 x 10^{-2} day^{-1}. The value of D obtained for no bed system was 35 x 10^{-2} day^{-1}.

5. CONCLUSIONS

Based on the findings of this study as the treatment of nitrogenous fertilizer wastes by the process of nitrification the following conclusions may be drawn.

1. The increase in surface area by providing more depth of sand bed will not help in achieving more nitrification as it is difficult to achieve mixing and uniform disperssion of reactants.

2. The value of maximum specific growth rate and saturation constant for NH_3-N oxidizing bacteria is 0.667 day^{-1} and 238 mg/l respectively.

3. The theortical postulation by Monod & Others (39) is applicable for a system having nitrifying bacteria in suspension.

4. In the recator having no supporting medium the nitrifying bacteria are active upto a dilution rate of 50 x 10^{-2} day^{-1} and beyond this dilution rate washout will occur.

5. The increase in surface area by providing the beds of packing straw results in improved in nitrification. The nitrification in a double bed reactor is 10% more than single bed system upto a dilution rate of 40 x 10^{-2} and beyond this dilution rate the nitrification in double bed reactor is nearly 50% more than single bed reactor.

6. The density of active nitrifying bacteria on the packing straw bed was observed to be 0.045 mg/sq.cm. for single bed system and 0.0457 mg/sq.cm. for double bed system.

7. The maximum nitrification/unit volume of reactor is at a dilution rate of 40 x 10^{-2} day^{-1} and 90 x 10^{-2} for a reactor having single bed, 50 x 10^{-2} day^{-1} and 120 x 10^{-2} day^{-1} for a reactor having double bed and 35 x 10^{-2} day^{-1} for a reactor having no supporting medium.

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